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(54) Ethylene-alpha-olefin copolymer composition.

(57) An ethylene-alpha-olefin copolymer composition comprising two ethylene-alpha-olefin copolymers which are different in density, intrinsic viscosity and the number of short chain branching per 1000 carbon atoms. Extrusion processed materials, injection molded materials and films obtained from said composition are excellent in strength.

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1 therefore, cause occasional troubles and are susceptible
to attack by chlorine water. Further, they are not
sufficient in creep characteristics, which makes them
unusable in pipes of high internal pressure. When high
5 pressure polyethylenes are used as coating materials for
steel pipes, their low temperature resistance is not
satisfactory, which makes their use in very cold climatic
areas improper. In their use as coating materials for
electric wires, troubles occur at times due to improper
10 environmental stress cracking resistance and water-tree
resistance.

To improve these defects, some attempts have
been proposed. However, their quality is still not in
a satisfactory level.

15 On the other hand, for improvement of these
defects, the following polymerization methods have been
adopted.

(1) Polymerization of ethylene and other polymerizable monomer such as vinyl acetate.

20 (2) Method in which ethylene and acrylic acid (or methacrylic acid) are polymerized followed by conversion to a salt with a metal, namely an ionomer.

The former method still has many problems such as (a) reduction of tear strength, rigidity and heat
25 resistance of films, (b) occurrence of corrosion of extruder and smell in processing due to liberation of acetic acid and (c) occurrence of blocking due to sticky film surface and cold flow. The latter method has

1 problems of reduction of thermal stability and weather -
resistance and of high cost.

Also for improvement of the defects of high pressure polyethylenes, there were made proposals in
5 which a high pressure polyethylene is mixed with an other α -olefin polymer such as high density polyethylene, polypropylene, polybutene, or a rubber. However, an improvement in one defect causes another problem and no satisfactory answer has been attained.

10 As resins which have low densities about equal to those of high pressure polyethylenes, there are known resins which are prepared by co-polymerizing ethylene and an α -olefin under a medium to low pressure using a transition metal catalyst. (Hereinafter, are abbreviated
15 as "ethylene- α -olefin copolymers"). The copolymers produced with a vanadium catalyst are low in degree of crystallization, and have problems in heat resistance, weather resistance and mechanical strengths. The ethylene- α -olefin copolymers produced under normal poly-
20 merization conditions with a titanium catalyst, having generally narrow molecular weight distributions (narrower than those of high pressure polyethylenes), are relative-
ly excellent in mechanical strengths but poor in melt rheology characteristics and have many problems in
25 processing. In blown film processing, a large quantity of electricity is needed, output is reduced or bubble stability is lost. In high speed processing, shark skin appears on film surfaces thereby losing product values.

1 Also in blow molding, parison stability is lost, or
surfaces of molded products turn to shark skin and pro-
duct values are lost. In injection molding, processing
temperatures need to be largely raised because of poorer
5 flow property under high pressures as compared with high
pressure polyethylenes, which requires more heat energy
and moreover causes resin deterioration.

Trials have been made in recent years for
solving these problems by improving extruders, screws
10 and dies. These approaches require a large amount of
expenditures and moreover techniques have not been fully
developed. Further, various other problems such as the
following:

(1) with respect to mechanical strengths of films
15 produced, balancing of machine direction (MD) and trans-
verse direction (TD) is difficult and the tear strength
of MD is poorer than that of high pressure polyethylenes,
and

(2) film transparency is inferior to that of high
20 pressure polyethylenes, because the ethylene- α -olefin
copolymer of narrow molecular weight distribution has a
faster crystallization speed than high pressure poly-
ethylenes and causes melt fracture more easily.

Low density ethylene- α -olefin copolymers are
25 difficult to obtain under normal polymerization conditions
using a chromium catalyst, because copolymerizability
between ethylene and α -olefin is generally lower with
chromium catalysts than with titanium catalysts. When

- 1 a chromium-titanium catalyst is used in order to overcome
this problem, ethylene- α -olefin copolymers obtained have
wider molecular weight distributions than copolymers
produced with a titanium catalyst and have slightly im-
5 proved processability. However, their mechanical strengths
largely worsen and their physical properties are not much
different from those of high pressure polyethylenes and
these copolymers provide film sheets and bottles inferior
in transparency.
- 10 For improving the transparency of these copoly-
mers, when the quantity of an α -olefin is largely
increased in polymerization and the density of a copoly-
mer obtained is reduced, only a sticky copolymer having
much deteriorated mechanical strengths is produced.
- 15 According to the knowledge of the present in-
ventors, ethylene- α -olefin copolymers polymerized under
a medium to low pressure using a transition metal cata-
lyst, have non-uniform component distributions. Namely
in these copolymers, the number of short chain branching
20 per 1000 carbon atoms (excluding methyl groups at the
ends) (hereinafter referred to as "S.C.B." for brevity)
varies depending upon molecular weight, and generally
lower molecular weight components have larger S.C.B. and
higher molecular weight components have smaller S.C.B.
- 25 This phenomenon is considered to be due to that α -olefins
tend to act as a chain transfer agent or act even to
active sites of catalyst to which molecular weight
regulators such as hydrogen tend to act. (cf. Reference

1 example 1.)

Because of the above phenomenon, ethylene- α -olefin copolymers polymerized with the α -olefin concentration increased with an aim to reduce to a large extent the density of copolymers produced, only give such products as those having increased S.C.B. in their lower molecular weight components thereby having increased solubility in solvents and poor mechanical strengths and causing surface stickiness. This tendency is particularly remarkable in those ethylene- α -olefin copolymers which are polymerized with a catalyst giving wider molecular weight distributions. One of the reasons for poor mechanical strengths of ethylene- α -olefin copolymers having wide molecular weight distributions will be explained by the above fact.

As described above, ethylene- α -olefin copolymers having densities about equal to those of high pressure polyethylenes and synthesized under a medium to low pressure with a transition metal catalyst, can not satisfy all of processability, mechanical strengths and transparency. For instance, lowering of molecular weight for improvement of processability results in large reduction in mechanical strengths and disappearance of said copolymer characteristics. Broadening of molecular weight distribution leads to large reduction in mechanical strengths as well (cf. Reference example 2.), and moreover transparency worsens and surfaces of molded products get sticky. Thus, both of processability and physical

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1 properties are not met together yet, and any low density
ethylene- α -olefin copolymer excellent in processability
and mechanical strengths have not yet been provided.

As described above, high pressure polyethylenes
5 are excellent in rheology characteristics and processa-
bility but relatively poor in mechanical strengths. On
the other hand, ethylene- α -olefin copolymers polymerized
under a medium to low pressure with a transition metal
catalyst and having densities about equal to those of
10 high pressure polyethylenes, have excellent mechanical
strengths due to their narrower molecular weight distri-
butions but are poor in processability. These property
differences are considered to originate from molecular
structures of polymers.

15 High pressure polyethylenes are obtained from
radical polymerization under a pressure of about 1500 to
4000 kg/cm² at a temperature of about 150° to 350°C in
an autoclave or a tubular reactor. Their molecular
structures are very complicated and, in spite of being
20 homopolymers of ethylene, have short chain branches
which are alkyl groups of 1 to 6 carbon atoms. These
short chain branches affect crystallinities and therefore
densities of polymers. The distribution of short chain
branching of high pressure polyethylenes is relatively
25 even, and both lower molecular weight components and
higher molecular weight components have almost similar
numbers of branches.

Another important feature of high pressure

1 polyethylenes is that the polyethylenes have also long
chain branches in complicated structures. Identification
of these long chain branches is difficult, but these
branches are considered to be alkyl groups of which
5 lengths vary from about lengths of main chains to lengths
having carbon atoms of over several thousands. The pre-
sence of these long chain branches largely affects melt
rheology characteristics of polymers and this is one of
the reasons for excellent processability of high pressure
10 method polyethylenes.

On the other hand, ethylene- α -olefin copolymers
synthesized under a medium to low pressure with a transi-
tion metal catalyst and having densities about equal to
those of high pressure polyethylenes, are obtained by co-
15 polymerizing ethylene and an α -olefin under a medium to
low pressure of about 5 to 150 kg/cm² and at 0° - 250°C
normally at a relatively low temperature of 30° to 200°C
with a transition metal catalyst in an autoclave or a
tubular reactor. Their molecular structures are relatively
20 simple. These ethylene- α -olefin copolymers seldom possess
long chain branches and have only short chain branches.
These short chain branches are not formed through compli-
cated reaction processes as so in high pressure poly-
ethylenes, but are controlled by the kind of an α -olefin
25 to be used in the copolymerization. As an example, in a
copolymerization between ethylene and butene-1, short
chain branches formed are normally ethyl branches. These
branches could be hexyl branches as a result of dimeriza-

1 tion of butene-1. Short chain branches formed control
crystallinities and densities of polymers.

Distribution of short chain branches is also
affected by the nature of a transition metal catalyst
5 used in the copolymerization, the type of polymerization
and the temperature of polymerization. Different from
the case of high pressure polyethylenes, the distribu-
tion is wide. Namely, as a general trend, lower molecular
weight components have larger S.C.B. and higher molecular
10 weight components have smaller S.C.B. (cf. Reference
exmaple 1.)

Ethylene- α -olefin copolymers obtained by copoly-
merizing ethylene and an α -olefin under a medium to low
pressure with a transition metal catalyst and having
15 densities about equal to those of high pressure poly-
ethylenes, have come to be practically used. Therefore,
the conventional classification that polyethylene resins
having densities of 0.910 to 0.935 g/cm³ fall in a ca-
tegory of high pressure polyethylenes, is improper and
20 a new classification should be developed mainly based on
whether or not a polymer or resin has long chain branches.
As low density polyethylenes substantially not having
long chain branches, there are resins which are obtained
by polymerization using a transition metal catalyst under
25 a same high pressure and temperature as employed in the
manufacture of high pressure method polyethylenes. These
resins are also included in "ethylene- α -olefin copolymers"
as defined by the present invention.

1 Presence or absence of long chain branches is
clarified to a considerable extent by a theory of solu-
tion. As an example, the presence of long chain branches
in an ethylene polymer can be known by using $[\eta]/[\eta]_g$
5 namely g^*_η . Herein, $[\eta]$ is the intrinsic viscosity of the
ethylene polymer, and $[\eta]_g$ is the intrinsic viscosity of
a reference linear polyethylene (high density poly-
ethylene produced from homopolymerization of ethylene
under a medium to low pressure with a Ziegler catalyst)
10 having the same weight average molecular weight by the
light scattering method. Molecules having more long
chain branches have less spread in a solution, and there-
fore, their g^*_η is small. Normally, g^*_η of high pressure
polyethylenes is 0.6 or less.

15 This method is useful, but practically presence
of long chain branches can be known more easily and
clearly by a correlation between melt index and intrinsic
viscosity of polymer. This correlation was shown in
Reference example 3. In there, the intrinsic viscosity
20 of a high pressure polyethylene is far lower than that
of the ethylene- α -olefin copolymer according to medium
to low pressure method having the same melt index,
because the former polyethylene has long chain branches.

25 Due to difference of presence or absence of
long chain branches, high pressure polyethylenes and
ethylene- α -olefin copolymers give largely differed
properties in melt rheology characteristics, crystallini-
ty, solid mechanical properties and optical properties.

1 The present inventors made strenuous efforts
with an aim to obtain polyethylenes which will solve the
above-mentioned defects of polyethylenes, will have
processability equal to or better than that of high
5 pressure polyethylenes, and will be excellent in tear
strength, impact strength, environmental stress cracking
resistance, low temperature resistance, creep character-
istics, chemicals resistance, transparency and heat-
sealing characteristics. As a result, the present in-
10 ventors have found that, by mixing (a) an ethylene- α -
olefin copolymer having a relatively higher molecular
weight and of which density, intrinsic viscosity, S.C.B.,
kind of α -olefin and (weight average molecular weight)/
(number average molecular weight) are specified and (b)
15 another ethylene- α -olefin copolymer having a relatively
lower molecular weight and of which density, intrinsic
viscosity, S.C.B., kind of α -olefin and (weight average
molecular weight)/(number average molecular weight) are
specified, in such a way that the ratio of S.C.B. of the
20 former copolymer over S.C.B. of the latter copolymer is
in a specified range, ethylene copolymer compositions can be
obtained which composition has extremely good processa-
bility compared with the conventional polyethylenes as
well as very excellent physical and chemical properties
25 such as tear strength, impact strength, environmental
stress cracking resistance, low temperature resistance,
creep characteristics, chemicals resistance, transparency,
and heat-sealing characteristics. The present inventors

1 have also found that ethylene- α -olefin copolymer compositions substantially not having long chain branches and having
5 a specific distribution of S.C.B. provide extremely good properties such as tensile strength, impact strength, environmental stress cracking resistance, low temperature
resistance, creep characteristics, chemicals resistance, transparency and heat-sealing characteristics, compared with the conventional polyethylenes, and therefore, with such
10 ethylene- α -olefin copolymer compositions, improvement of processability by broadening of molecular weight distribution can be attained without deterioration of properties described above. Thus, the present invention has been achieved.

According to the present invention, there is provided an ethylene- α -olefin copolymer composition excellent in strength and having a density of 0.910 to 15 0.940 g/cm³, a melt index of 0.02 to 50 g/10 min. and a melt flow ratio of 35 to 250, which comprises 10 to 70% by weight of an ethylene- α -olefin copolymer A and 90 to 30% by weight of an ethylene- α -olefin copolymer B; said 20 copolymer A being a copolymer of ethylene and an α -olefin of 3 to 18 carbon atoms and having a density of 0.895 to 0.935 g/cm³, an intrinsic viscosity of 1.2 to 6.0 dl/g, and the number of short chain branching per 1000 carbon atoms (S.C.B.) of 7 to 40; said copolymer B 25 being a copolymer of ethylene and an α -olefin of 3 to 18 carbon atoms and having a density of 0.910 to 0.955 g/cm³, an intrinsic viscosity of 0.3 to 1.5 dl/g, and S.C.B. of 5 to 35; said copolymer A and said copolymer

1 B being selected in order to satisfy a condition that
5 (S.C.B. of said copolymer A)/(S.C.B. of said copolymer
B) is at least 0.6.

The present invention also provides a composition of copolymers of ethylene and an α -olefin of 3 to
5 18 carbon atoms, having the following properties:

- (1) density of 0.910 to 0.940 g/cm³,
- (2) intrinsic viscosity $[\eta]$ of 0.7 to 4.0 dl/g,
- (3) melt index of 0.02 to 50 g/10 min,
- 10 (4) the number of short chain branching per 1000 carbon atoms (S.C.B.) being 5 to 45,
- (5) $[\eta]/[\eta]_L$ namely g^*_η being at least 0.8, where $[\eta]_L$ is an intrinsic viscosity of a linear polyethylene having the same weight average molecular weight measured
15 by a light scattering method, and
- (6) (S.C.B. of the higher molecular weight components)/(S.C.B. of the lower molecular weight components) being at least 0.6, wherein these two component groups are obtained by a molecular weight fractionation method.

20 The first feature of this invention is to provide an ethylene copolymer composition of which processability is about equal to or better than that of high pressure polyethylenes and of which physical and chemical properties such as tensile strength, impact strength, environmental stress cracking resistance,
25 creep characteristics, tear strength, transparency, heat-sealing characteristics and chemicals resistance are very excellent.

1 The second feature of this invention is that,
because the product of this invention is excellent in
mechanical strengths, has a rigidity higher than those
of high pressure polyethylenes and has a transparency
5 about equal to that of high pressure polyethylenes,
material saving can be expected with the product of this
invention; for instance, when this product is used for
films, the same performance can be obtained with the
thickness 10 to 20% thinner than that of high pressure
10 polyethylenes.

The third feature of this invention is that,
because the product of this invention has extrusion
processability superior to that of relatively low density
ethylene- α -olefin copolymers by the conventional
15 technique, conventional extruders being used for high
pressure polyethylenes can be utilized for the present
product without any modification.

The fourth feature of this invention is that,
because the present product, even if possesses a melt
20 index lower than those of low density ethylene- α -olefin
copolymers by the conventional technique, shows satisfactory
flow properties in actual processing, it gives
excellent bubble stability and mechanical strengths of
machine and transverse directions can be easily balanced,
25 whereby molded products can have a uniform quality.

The fifth feature of this invention is that,
because a resin composition less sticky than low density
ethylene- α -olefin copolymers by the conventional

1 technique is obtained even when the density of the composition is lowered, the composition can be applied even for the usages where transparency, flexibility and impact characteristics are required.

5 In the attached drawings, Figs. 1 to 6 show curves of molecular weight distributions obtained from gel permeation chromatography. Broken lines in these figures are for dividing lower molecular weight components and higher molecular weight components into two respective
10 territories.

Fig. 7 is a typical example showing "distribution of S.C.B. against molecular weight" of an ethylene- α -olefin copolymer of the conventional technique.

Fig. 8 shows correlations between melt indices
15 (MI) and tensile impact strengths of ethylene- α -olefin copolymers of the conventional technique, with their melt flow ratios (MFR) used as a parameter.

Fig. 9 shows correlations between MI and intrinsic viscosities [η] of a high pressure polyethylene
20 and a linear polyethylene of the medium to low pressure method as a method for distinguishing these two polymers.
In the figure, a broken line is drawn to separate two territories, the left side territory is for the high pressure polyethylene of the conventional technique and
25 the right side territory is for the linear polyethylene of the medium to low pressure method.

The present invention will be explained in more detail below.

- 1 An ethylene- α -olefin copolymer of a relatively,
high molecular weight (hereinafter referred to as "co-
polymer A") which is used in the present invention as
one mixing component, is a copolymer of ethylene and an
5 α -olefin of 3 to 18 carbon atoms. This α -olefin is a
one represented by a general formula R-CH=CH₂ wherein R
is an alkyl group of 1 to 16 carbon atoms. Examples of
the α -olefin include propylene, butene-1, pentene-1,
hexene-1, heptene-1, octene-1, nonene-1, decene-1, 4-
10 methyl-pentene-1, 4-methyl-hexene-1 and 4, 4-dimethyl-
pentene-1. Among these olefins, α -olefins of at least
4 carbon atoms are preferred. Particularly, butene-1,
pentene-1, hexene-1, octene-1 and 4-methyl-pentene-1 are
preferred from the standpoints of monomer availability,
15 copolymerizability and quality of polymer obtained.
These α -olefins can be used alone or in combination of
two or more. The density of the copolymer A is influenced
by the kind of an α -olefin used, the content of the
olefin and the intrinsic viscosity of the copolymer.
20 For the object of this invention, the density is required
to be 0.895 to 0.935 g/cm³ and more preferably 0.895 to
0.930 g/cm³. In the density smaller than 0.895 g/cm³,
copolymers stick to the reactor walls causing polymeri-
zation difficult, or, the density of the relatively
25 lower molecular weight copolymer (namely "copolymer B"
which is described later and used as another mixing
component in the present invention) is required to be
raised, resulting in formation of polymer compositions

1 of undesirable qualities such as films of poor trans-
parency. In the density higher than 0.930 g/cm^3 , the
content of the α -olefin in the copolymer A becomes very
low, and the copolymer A of such a high density does
5 not give satisfactory mechanical strengths. For instance,
in films, balancing of MD and TD strengths becomes
difficult and heat-sealing characteristics get worse.
S.C.B. in the copolymer A is preferably 7 to 40 and more
preferably 10 to 40. (When R in the above α -olefin
10 formula is a linear alkyl group, the number of methyl
groups at branch ends per 1000 carbon atoms is S.C.B.
When R is an alkyl group with a branch or branches, for
instance, the α -olefin is 4-methyl-pentene-1, the branch
. is isobutyl group and the half number of methyl groups
15 at the branch ends is S.C.B.) Short chain branching in
ethylene- α -olefin copolymers occurs due to α -olefins and
it hinders crystallization mainly of ethylene sequences
and lowers densities. These effects vary depending upon
the kind of α -olefin. Short chain branching is con-
20 sidered to also make some contribution to formation of
interlamella molecules, and ultimately affects mechanical
strengths and thermal properties of copolymers obtained.
Therefore, when S.C.B. is below 7, mechanical strengths
and heat-sealing properties of the composition become
25 poor. For instance, in films, balancing of MD and TD
strengths is difficult. When S.C.B. is over 40, there
occur problems in polymerization of the copolymer A and
also the transparency of polymer compositions obtained

1 from the copolymer becomes poor.

The molecular weight of the copolymer A is generally preferred to be 1.2 to 6.0 dl/g as intrinsic viscosity and more preferred to be 1.2 to 4.5 dl/g.

5 When the intrinsic viscosity is below 1.2 dl/g, mechanical strengths of polymer compositions of the present invention are reduced. In over 6.0 dl/g, mixing with the copolymer B becomes difficult, and polymer compositions obtained have fish eyes and further

10 worsened flow properties as well as reduced transparency.

In injection molding, the intrinsic viscosity is preferably 1.2 to 4.0 dl/g and more preferably 1.2 to 3.0 dl/g. If it is less than 1.2 dl/g, mechanical strengths of compositions are lowered. If it is over 4.0 dl/g,

15 mixing with the copolymer B becomes insufficient, and polymer compositions obtained have Fish eyes, deteriorated flow properties (tend to cause flow marks) and reduced transparency.

(Weight average molecular weight)/(number

20 average molecular weight) of the copolymer A which is a measure for the molecular weight distribution of the copolymer obtained from gel permeation chromatography (hereinafter abbreviated as "GPC"), is preferably 2 to 10 and more preferably 3 to 8. If it is less than 2,

25 such a copolymer A is difficult to produce. If it is over 10, polymer compositions have lower mechanical strengths and, when processed into films, cause blocking.

An ethylene- α -olefin copolymer of a relatively

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1 low molecular weight (hereinafter abbreviated as "co-
polymer B") which is used in the present invention as
another mixing component, is a copolymer of ethylene and
an α -olefin of 3 to 18 carbon atoms. As α -olefins, there
5 may be selected from α -olefins used in the copolymer A.
The density of the copolymer B is normally preferred to
be 0.910 to 0.955 g/cm³. More preferably, it is 0.915
to 0.953 g/cm³. When the density is below 0.910 g/cm³,
copolymer compositions possess reduced mechanical streng-
10 ths and cause blocking due to bleeding of lower molecular
weight components of low density on film surfaces. When
the density is over 0.955 g/cm³, copolymer compositions
of this invention possess worsened transparency and too
high densities. In the area of injection molding, the
15 density of the copolymer B is preferred to be 0.910 to
0.950 g/cm³ and more preferred to be 0.915 to 0.948 g/cm³.
When the density is below 0.910 g/cm³, mechanical streng-
ths of compositions are reduced and surface tackiness
occurs. When the density is over 0.950 g/cm³, composi-
20 tions have too high densities. S.C.B. of the copolymer
B is preferred to be 5 to 35 and more preferred to be
7 to 30. When S.C.B. is below 5, the copolymer B has a
lower molecular weight as a whole and its crystalliza-
tion speed is fast, resulting in poor transparency of
25 compositions. In case of over 35, reduction in mechani-
cal strengths as well as blocking in films occurs.

The molecular weight of the copolymer B is 0.3
to 1.5 dl/g preferably 0.4 to 1.5 dl/g as intrinsic

1 viscosity. When the intrinsic viscosity is less than
0.3 dl/g, mechanical strengths and transparency of com-
positions are reduced. In case of over 1.5 dl/g,
fluidity of compositions is poor. In the area of injec-
5 tion molding, the molecular weight of the copolymer B
is preferably 0.3 to 1.2 dl/g as intrinsic viscosity
and more preferably 0.4 to 1.2 dl/g. When the intrinsic
viscosity is below 0.3 dl/g, mechanical strengths and
transparency of compositions are reduced. In case of
10 over 1.2 dl/g, fluidity of compositions is poor.

The value of (weight average molecular weight)/
(number average molecular weight), namely, \bar{M}_w/\bar{M}_n of the
copolymer B determined by gel permeation chromatography
(GPC) is preferably 2 to 10 and more preferably 3 to 8.
15 When \bar{M}_w/\bar{M}_n is below 2, the copolymer B is difficult to
produce. In case of over 10, mechanical strengths of
compositions are reduced and surface tackiness of films
occurs.

The copolymer A and the copolymer B as men-
20 tioned above can be obtained by copolymerizing ethylene
and an α -olefin of 4 to 18 carbon atoms under a medium
to low pressure using a transition metal catalyst.
For instance, catalysts such as Ziegler type catalyst
25 and Phillips type catalyst as well as polymerization
methods such as slurry polymerization, gas phase poly-
merization and solution polymerization are used. As
catalysts, a Ziegler type catalyst system using a
carrier-supported Ziegler catalyst component is

1 convenient in this invention from its activity and co-polymerizability. Specific examples of an effective carrier of this carrier-supported Ziegler catalyst component include oxides, hydroxides, chlorides and
5 carbonates of metals and silicon and their mixtures as well as inorganic complexes. More specifically, they are magnesium oxides, titanium oxides, silica, alumina, magnesium carbonates, divalent metal hydroxychlorides, magnesium hydroxides, magnesium chlorides, magnesium alkoxides, magnesium haloalkoxides, double oxides of magnesium and aluminum and double oxides of magnesium and calcium. Among these compounds, magnesium compounds are particularly preferred. The following magnesium compounds are particularly preferred. The following
10 magnesium compound carrier is most preferred in the production of the low density polyethylene type resin composition of this invention, because it gives a satisfactory slurry with no abnormal tackiness and there occurs no sticking of polymers to the reactor wall.
15 (Reference is made to Japanese Patent Publication No. 23561/1980.) Namely, it is the carrier obtained by (a) reacting in a solvent an aluminum halide represented by the general formula R_nAlX_{3-n} (R is an alkyl, aryl or alkenyl group of 1 to 20 carbon atoms and X is a halogen atom and n is an integer of 0 to 3) and/or a silicon
20 halide represented by the general formula $R_m^{\prime}SiX_{4-m}$ (R' is an alkyl, aryl or alkenyl group of 1 to 20 carbon atoms and X is a halogen atom and m is an integer of 0
25 to 4).

1 to 4) with an organomagnesium compound represented by the general formulas $R''MgX$ and/or $R_2''Mg$ (R'' is an alkyl, aryl or alkenyl group of 1 to 20 carbon atoms and X is a halogen atom), and (b) isolating the solid product
5 formed.

As a transition metal catalyst component supported on carriers, there are, for instance, titanium compounds, vanadium compounds and zirconium compounds. Their specific examples are titanium tetrachloride,
10 titanium tetrabromide, titanium tetraiodide, titanium trichloride, titanium alkoxy halides or titanium aryloxy halides represented by the general formula $Ti(OR^1)_{4-p}X_p$ (where R^1 is a hydrocarbon group, X is a halogen atom and p is an integer of $0 < p < 4$), vanadium tetra-
15 chloride, vanadium oxy trichloride, zirconium tetra-chloride and zirconium alkoxy halides or zirconium aryloxy halides represented by the general formula $Zr(OR^2)_{4-q}X_q$ (where R^2 is a hydrocarbon group, X is a halogen atom and q is an integer of $0 < q < 4$). Among
20 these compounds, titanium compounds and/or vanadium compounds are particularly preferred in the production of the low density polyethylene type resin composition of this invention, because they give satisfactory slurries with no abnormal tackiness and there occurs almost no
25 sticking of polymers to the reactor wall. (Reference is made to Japanese Patent Publication No.23561/1980.) Titanium compounds are most preferred from the standpoints of weather resistance and heat resistance.

1 As a component of carrier-supported Ziegler
catalysts used in this invention, there are also reaction
products between an organomagnesium compound and a
transition metal compound. Here, the transition metal
5 compound is represented by the general formula
 $Ti(OR^3)_{4-r}X_r$ (where R^3 is a hydrocarbon group, X is a
halogen atom and r is an integer of $0 \leq r \leq 4$, and
includes titanium tetrahalides, titanium alkoxides,
titanium aryloxides, titanium alkoxy halides and titanium
10 aryloxy halides.

As an organometal compound component which
forms the catalyst system of this invention together with
the carrier-supported Ziegler catalyst component, there
are organoaluminum compounds such as trialkyl aluminums
15 (triethyl aluminum, tri-n-propyl aluminum, tri-i-butyl
aluminum, tri-n-butyl aluminum, tri-n-hexyl aluminum,
etc.), dialkyl aluminum monohalides (diethyl aluminum
monochloride, di-n-propyl aluminum monochloride, di-i-
butyl aluminum monochloride, di-n-butyl aluminum mono-
20 chloride, di-n-hexyl aluminum monochloride, etc.), alkyl
aluminum dihalides (ethyl aluminum dichloride, n-propyl
aluminum dichloride, i-butyl aluminum dichloride, n-butyl
aluminum dichloride, n-hexyl aluminum dichloride, etc.),
ethyl aluminum sesquichloride, i-propyl aluminum sesqui-
25 chloride, i-butyl aluminum sesquichloride, n-butyl
aluminum sesquichloride and n-hexyl aluminum sesqui-
chloride as well as other organometal compounds such as
organozinc compounds. These organometal compounds may

1 be used alone or in combination of two or more.

In compounding the composition of this invention using the ethylene- α -olefin copolymer A of relatively higher molecular weight and the ethylene- α -olefin 5 copolymer B of relatively lower molecular weight both of which are obtained with the above catalyst system under a normal medium to low pressure polymerization method, the following matters must be obeyed.

(1) From the standpoint of mechanical strengths,

10 the copolymers A and B must be selected in order that (S.C.B. of copolymer A)/(S.C.B. of copolymer B) becomes at least 0.6, preferably at least 0.8 and more preferably at least 1.0. Meanwhile, from the standpoint of transparency, it is necessary that (S.C.B. of copolymer 15 A)/(S.C.B. of copolymer B) is 0.6 to 1.7. When this ratio is below 0.6, mechanical strengths of the copolymer composition obtained is reduced. In films, for instance, balancing of MD and TD strengths is difficult, heat-sealing characteristics worsen and tackiness is seen.

20 In case of over 1.7, transparency of the copolymer composition is reduced.

(2) The density of the copolymer composition is normally preferred to be 0.910 to 0.940 g/cm³ and more preferred to be 0.915 to 0.935 g/cm³ and most preferred 25 to be 0.915 to 0.929 g/cm³. When the density is below the above lower limit, mechanical strengths of the composition is reduced and, in case of films, tackiness is seen. When the density is above the upper limit, transparency of the composition worsens.

1 In the field of extrusion processing, the
density of the copolymer composition is preferred to be
0.910 to 0.930 g/cm³ and more preferred to have 0.915 to
0.929 g/cm³. When the density is below the lower limit,
5 mechanical strengths of the composition is reduced and
products have tackiness. When the density is above the
upper limit, transparency worsens.

In the field of film processing, the density of
the copolymer composition is preferred to be 0.910 to 0.940
10 g/cm³ and more preferred to be 0.915 to 0.935 g/cm³ and most
preferred to be 0.915 to 0.929 g/cm³. When the density is
below the lower limit, mechanical strengths of the compo-
sition is reduced and films possess tackiness. When the
density is above the upper limit, transparency worsens.

15 In the filed of injection molding, the density
of the copolymer composition is preferred to be 0.910 to
0.935 g/cm³ and more preferred to be 0.915 to 0.929
g/cm³. When the density is below the lower limit,
mechanical strengths of the composition is reduced and
20 molded products have tackiness. When the density is
above the upper limit, transparency worsens.

(3) The melt index of the copolymer composition is
normally preferred to be 0.02 to 50 g/10 min. and more
preferred to be 0.05 to 40 g/10 min. and most preferred
25 to be 0.1 to 30 g/10 min. In addition, the melt flow
ratio is preferred to be 35 to 250 and more preferred
to be 35 to 200 and most preferred to be 35 to 150.
Furthermore, the product of the melt index and the

1 melt flow ratio is preferred to be at least 4 and
more preferred to be at least 7. When the melt index
and the melt flow ratio are below the lower limits,
extrusion processability worsens. When they are above
5 the upper limits, bubble stability in blown film proces-
sing is lost and mechanical strengths are reduced.

In the field of extrusion processing, the MI
of the copolymer composition is preferred to be 0.02 to
2.0 g/10 min. and more preferred to be 0.05 to 2.0 g/
10 10 min. and most preferred to be 0.10 to 2.0 g/10 min.
Further, the MFR is preferred to be 35 to 250 and more
preferred to be 35 to 200 and most preferred to be 35 to
150. Furthermore, the product of MI and MFR is preferred
to be at least 4 and more preferred to be at least 7.
15 When the MI and the MFR are below the lower limits,
extrusion processability worsens. When they are above
the upper limits, mechanical strengths are reduced.

In the field of film processing, the MI of the
composition is preferred to be 0.02 to 5 g/10 min. and
20 more preferred to be 0.05 to 4 g/10 min. and most pre-
ferred to be 0.1 to 3 g/10 min. Further, its MFR is
preferred to be 35 to 250 and more preferred to be 35 to
200 and most preferred to be 35 to 150. Furthermore,
the product of the MI and the MFR is preferred to be
25 at least 4 and more preferred to be at least 7. When
the MI and the MFR are below the lower limits, extrusion
processability worsens. When they are above the upper
limits, bubble stability in blown film processing is

1 insufficient and mechanical strengths are reduced.

In the field of injection molding, the MI of the composition is preferred to be 2.0 to 50 g/10 min. and more preferred to be 2.0 to 30 g/10 min. Further, 5 the MFR is preferred to be 35 to 80 and more preferred to be 35 to 70. When the MI is below the lower limit, moldability worsens and flow marks are produced. When it is above the upper limit, mechanical strengths are reduced.

10 In order to provide the composition of this invention excellent in processability and mechanical strengths, it is also important to adequately balance its MI and MFR. A lower MI requires a higher MFR. This requirement is expressed by the product of MI and MFR. 15 For instance, a composition having a MI of about 1 g/10 min, even if its MFR is as low as 50 to 60, has processability about equal to that of a high pressure polyethylene having the same MI. On the other hand, a composition having a MI of about 0.05 g/10 min. 20 and a MFR of 50 possesses extremely poor processability and, in order to have satisfactory processability, a MFR of at least 80 is required. The product of MI and MFR of a composition is designed appropriately to meet the requirement of its final application. The designed 25 value of the product of MI and MFR can be achieved in the composition by using (a) intrinsic viscosities of the copolymer A of relatively higher molecular weight, and the copolymer B of relatively lower molecular weight,

- 1 (b) values of (weight average molecular weight)/(number average molecular weight) of these copolymers and (c) their mixing ratio. If intrinsic viscosities of the copolymer A and the copolymer B are put as $[\eta]_A$ (dl/g)
- 5 and $[\eta]_B$ (dl/g), respectively, and their ratios by weight basis are put as w_A and w_B ($w_A + w_B = 1$), respectively the intrinsic viscosity of the composition obtained by mixing the two copolymers namely $[\eta]_T$ (dl/g) is approximately given by the following formula.

10

$$[\eta]_T = [\eta]_A w_A + [\eta]_B w_B$$

- MI is governed by $[\eta]_T$ unequivocally. Meanwhile, MFR is generally larger when $[\eta]_A / [\eta]_B$ is larger, and depends upon w_A and w_B . Therefore, it is difficult to express MFR unequivocally and, based on preliminary tests, $[\eta]_A$,
- 15 $[\eta]_B$, w_A and w_B are determined to give an intended MFR.
- (4) In order to obtain a composition which satisfy the above (1) to (3) conditions, the copolymer A and the copolymer B are preferred to be mixed at a ratio of 10 to 70% by weight (copolymer A) to 90 to 30% by weight
- 20 (copolymer B). The ratio of 20 to 65% by weight to 80 to 35% by weight is more preferred and the ratio of 30 to 60% by weight to 70 to 40% by weight is most preferred. The mixing ratio of the two copolymers must be adequately selected by considering S.C.B., densities, intrinsic
- 25 viscosities and molecular weight distributions of the copolymers A and B as well as the density, MI and MFR

1 of an intended composition. When the ratio of the
copolymer A is below its lower limit and the ratio of the
copolymer B is above its upper limit, the ESCR, impact
strength, tear strength and low temperature resistance
5 of the composition obtained are poor, and the high
strength of the composition of this invention which is
obtained when the value of (S.C.B. of copolymer A)/(S.C.B.
of copolymer B) is selected to be at least 0.6 as well
as the good transparency of the composition of this
10 invention which is obtained when the value of (S.C.B. of
copolymer A)/(S.C.B. of copolymer B) is selected to be
0.6 to 1.7, are not achieved. When the ratio of the
copolymer A is above its upper limit and the ratio of
the copolymer B is below its lower limit, the processa-
15 bility of the composition obtained worsens.

As long as the scope of this invention is
obeyed, mixing of the ethylene- α -olefin copolymer A of
relatively higher molecular weight and the ethylene- α -
olefin copolymer B of relatively lower molecular weight
20 is not necessarily limited to mixing of each one kind.
The mixing may be also done by using each two or more
kinds of the copolymer A and the copolymer B.

There is no particular limitation to mixing
methods of the copolymers A and B, and known methods can
25 be used in mixing of these two polymers. Commonly used
are a batch type melt kneading method which employs a
twin roll or a Banbury mixer after separate production
of the copolymers A and B, a continuous melt kneading

1 method employing a twin rotor mixer such as CIM (manufactured by the Japan Steel Works) or FCM (manufactured by Kobe Steel) or a single screw extruder and a solution mixing method in which a mixture is obtained by dissolving the copolymers A and B in a solvent separately or together, blending and finally removing the solvent.

When the copolymers A and B are produced by a high temperature solution polymerization method, it is advantageous from the process standpoint that their

10 composition is obtained by mixing A and B in a solution state at high temperatures and removing the solvent.

Mixing by a two- or multi-stage polymerization method is also possible. In this method, in the first stage, the copolymer A is polymerized for a certain length of time and, successively in the second stage, the copolymer B is polymerized using the same catalyst but changing other polymerization conditions until the composition containing the copolymers A and B at an intended ratio is obtained. In this case, the order of

20 polymerization of A and B is not restricted.

The above two- or multi-stage polymerization method is an ideal mixing method, because the copolymers A and B undergo molecular dispersion.

The most effective mixing method can be selected from above various mixing methods, in order to obtain a uniform composition, which meets intended requirements.

The intrinsic viscosity $[\eta]$ of the ethylene- α -

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1 olefin copolymer composition of this invention is preferred to be 0.7 to 4 dl/g and more preferred to be 0.8 to 3.5 dl/g and most preferred to be 0.9 to 3 dl/g. When the intrinsic viscosity is below the lower limit, 5 mechanical strengths are reduced and, in blown film processing, bubble stability is insufficient. In case of above the upper limit, extrusion processability worsens.

S.C.B. of the composition is preferred 10 to be 5 to 45 and more preferred to be 7 to 40 and most preferred to be 10 to 40. When S.C.B. is below its lower limit, transparency worsens. When S.C.B. is above its upper limit, mechanical strengths are reduced and molded products have tackiness.

15 Next, the "index of long chain branching" of the copolymer composition of this invention is described. When the intrinsic viscosity of a copolymer composition of this invention is put as $[\eta]$ and the intrinsic viscosity of a linear polyethylene having the same \bar{M}_w measured by 20 light scattering method (a high density polyethylene obtained by homopolymerization of ethylene under a medium to low pressure using a Ziegler catalyst) is put as $[\eta]_L$, $[\eta]/[\eta]_L$ namely g^*_η is called the "index of long chain branching" of the composition and indicates the extent 25 of presence of long chain branching in the composition. Now, intrinsic viscosities of two polymers are compared. One polymer X is a polyethylene having long chain branches of which index of branching is unknown (for

1 instance, a high pressure polyethylene) and the other
polymer is a linear polyethylene containing no long
chain branches but having the same \bar{M}_w measured by light
scattering method. When these two polymers are made into
5 respective very dilute solutions with one same solvent,
the polymer X gives a less-viscous solution because the
spread of its molecular chain is smaller than that of the
linear polyethylene. Accordingly, by measuring the
intrinsic viscosities of the two polymers and calculating
10 their ratio namely g_{η}^* , the index of long chain branching
can be known. When a polymer has no long chain branches,
its g_{η}^* is almost 1 within the range of experimental
errors. When the polymer has long chain branches, g_{η}^* is
smaller than 1. In most cases, high pressure polyethylenes
15 show g_{η}^* of below 0.6 and have considerable quantities of
long chain branches.

The ethylene- α -olefin copolymer composition of
this invention is preferred to have g_{η}^* of at least 0.8
and more preferably at least 0.9 and practically has no
20 long chain branches. When g_{η}^* is below 0.8 and contain
a large quantity of long chain branches, the copolymer
is poor in tensile strength, impact strength, environ-
mental stress cracking resistance, low temperature
resistance and chemicals resistance.

25 (S.C.B. of higher molecular weight components)/
(S.C.B. of lower molecular weight components) of the
copolymer composition of this invention is preferred to
be at least 0.6 and more preferred to be at least 0.8

1 and most preferred to be at least 1.0. In applications
where transparency is required, 0.6 to 0.8 is preferred.
Here, these S.C.B. are obtained by dividing the compo-
sition of this invention into two groups of lower mole-
5 cular weight components and higher molecular weight
components using molecular weight fractionation and then
measuring S.C.B. of each group. When the ratio is below
0.6, mechanical strengths of the composition are poor,
and when the composition is subjected to extrusion proces-
10 sing and injection molding, balancing of MD and TD
strengths is difficult and molded products have sticky
surfaces, and in films, heat-sealing characteristics
worsen. When the ratio is over 0.8, transparency worsens
and therefore such a polymer is not suitable for appli-
15 cations where transparency is required. The above mole-
cular weight fractionation of the ethylene- α -olefin
copolymer into two groups of lower and higher molecular
weight components refers to the following method.

(1) A curve of molecular weight distribution is
20 obtained by gel permeation chromatography.

In this case, the abscissa is the logarithm of
chain length (unit Å) calibrated with a standard poly-
styrene sample, and the ordinate is relative weight
fraction. The standard measurement method is described
25 later.

(2) An example of cases where curves of molecular
weight distributions have one peak was shown in Fig. 1.
This pattern is seen most typically in ethylene- α -olefin

1 copolymers. In this case, a lower molecular weight
components side and a higher molecular weight components
side are divided by a line drawn between the peak of the
curve and the midpoint of a line drawn between the end
5 of lower molecular weight components in the curve and
the end of higher molecular weight components; and the
ratio of areas of these two sides is the weight ratio of
lower and higher molecular weight components. Separately,
fractions of the same sample are prepared by column
10 fractionation. These fractions are consolidated into
two portions of lower and higher molecular weight com-
ponents, in order that the weight ratio of these two
portions become closest to the weight ratio obtained
above.

15 (3) An example of cases where curves of molecular
weight distributions have two peaks was shown in Fig. 2.
Also, an example having one peak but showing a shoulder
at higher molecular weight components side was shown in
Fig. 3. Examples having three or more peaks are handled
20 as modifications of two peaks and are treated similarly
to two peaks. In the case of two or more peaks including
shoulders, a tangent line is drawn between main two peaks
of the higher molecular weight components side or between
one peak and a shoulder of the same side, and then a
25 perpendicular is drawn from a point where the distance
between the GPC curve and the tangent line becomes largest.
This perpendicular splits the lower molecular weight
components side and the higher molecular weight components

1 side, and the ratio of areas of these two sides becomes
the weight ratio of these two components portions. When
peaks are continuous and can not be detected (case of
somewhat square curve), the technique of one peak
5 distribution is applied. Separately, fraction of the
same sample are prepared by column fractionation. These
fractions are consolidated into two portions of lower
and higher molecular weight components, in order that
the weight ratio of these two portions becomes closest
10 to the weight ratio thus obtained.

Molecular weight fractionation is conducted by
the known column fractionation method. Its detailed
explanation is made in "Polymer Fractionation" (compiled
by M.J.R. Cantow, Academic Press, published in 1967),
15 and therefore, only the outline of the method is described
below.

About 5 g of a sample is adsorbed on a carrier,
Celite 745, in xylene and the carrier is charged into a
column. The column is heated to 130°C and a mixed solvent
20 of butyl cellosolve and xylene is passed through the
column with their mixing ratio being gradually changed
(namely with the solvency of the mixed solvent being
gradually changed). This lower molecular weight fractions
to higher molecular weight fractions are successively
25 fractionated. To each eluate is added methanol to cause
precipitation. After recovery of each polymer, they are
dried under reduced pressure to be used as each fraction.
To prevent the decomposition of polymers during

1 fractionation, 100 ppm of Irganox® 1076 is added to
the original sample as a stabilizer, and also nitrogen
is passed through the column to shut off oxygen. The
polymer fractions obtained are divided into two groups
5 of lower and higher molecular weight components so that
the weight ratio of these two groups become the above-
mentioned weight ratio. Each group is made into a press
sheet of about 100 to 300μ thickness and these sheets
are subjected to Fourier-transform infra-red absorption
10 spectroscopy.

Further, it is preferable that the characteristic values of the sample obtained by dividing the ethylene- α -olefin copolymer of this invention into two fractions such as a higher molecular weight component
15 and a lower molecular weight component are same to the characteristic values of copolymer A and copolymer B, respectively, as previously defined.

When compared with low density ethylene- α -olefin copolymers obtained from the conventional medium
20 to low pressure method (normally called "linear low density polyethylene or LLDPE"), the polyethylene type resin composition of this invention has the following advantages.

In the field of extrusion processing, the composition of this invention is largely excellent in
25 processability (about equal even to high pressure polyethylenes) and moreover has excellent mechanical strengths (ESCR, tensile strength, impact strength and

1 tear strength) as well as excellent low temperature
resistance. Therefore, reduction in thicknesses of
molded products becomes possible. The composition of
this invention has wide applications and can be used.
5 even in the application where transparency is required.

In case of films, the present composition is
far superior in processability (about equal even to high
pressure polyethylenes). Further, the composition has
excellent mechanical strengths such as tensile strength,
10 impact strength and tear strength, by which reduction
in thicknesses of films becomes possible. Moreover, the
present composition has excellent transparency and heat-
sealing characteristics, by which it is used as a high
quality film in wide applications including high speed
15 bag manufacturing.

In the field of injection molding, the present
composition is largely excellent in processability (about
equal even to high pressure polyethylenes). Moreover,
there occurs no flow marks, there is no warpage with
20 molded products, and transparency, low temperature
resistance and mechanical strengths such as environmental
stress cracking resistance, tensile strength and impact
strength are excellent. Thereby, reduction in thicknesses
of molded products is possible and the present composition
25 has wide applications including the case where transparency
is required.

To the composition of this invention, can be
added if necessary various additives being commonly used

1 in the industries such as oxidation inhibitors, lubricants, anti-blocking agents, anti-static agents, photostabilizers, and coloring pigments. Also, other polymers can be added in small quantities as long as the scope of this invention
5 is kept.

Next, the definitions of physical and chemical properties used in this invention are explained below.

(1) Intrinsic viscosity

This implies $[\eta]$ in tetralin of 135°C.

10 $[\eta] = 11.65 \times \log R$

$$R = t/t_0$$

t : Seconds of dropping in a concentration of
0.2. dl/g

t_0 : Seconds of dropping of tetralin itself

15 (2) Density

According to the specification in JIS-K-6760.

With respect to the copolymer B of lower molecular weight, when it has a large S.C.B., it is regarded as a low density product, and according to the specification, it must be subjected to annealing of 100°C and 20 1 hour. However, the copolymer B was conformed in all cases to the specification for high density products and was not subjected to the above annealing.

(3) S.C.B.

25 Using the C₁₄ labelled product described in the following literature, the subject property was calculated by employing the FT-IR spectrum subtraction method.

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1

"Characterization and Properties of Polymers"

Published by KAGAKU DOJIN

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Pages 131 to 146

Determination formulas for various branches are given
below.

| Branch | Determination formula |
|---------------------|---------------------------------|
| Methyl | Branches/1000 C = 0.49·K 7.25 μ |
| Ethy1 | " = 0.70·K 7.25 μ |
| n-Butyl | " = 0.80·K 7.25 μ |
| n-Decyl | " = 0.78·K 7.25 μ |
| Other linear chains | " = 0.80·K, 7.25 μ |
| 1-Butyl | " = 0.45·K 7.23 μ |

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1 - $K_{7.25\mu}$ (absorptivity) was obtained by using as
a reference a linear ethylene homopolymer having the
almost same molecular weight and molecular weight distri-
bution and the same $[\eta]$ as those of a given sample and
5 employing the spectrum subtraction method. Therefore,
effects of methyl groups at the ends were cleared.

When R of an α -olefin $R-CH=CH_2$ is a linear
alkyl, (the number of methyl groups at the branch ends)/
1000C is S.C.B. When R is a branched alkyl group, for
10 instance, an α -olefin is 4-methyl-pentene-1, the branch
is the i-butyl group and half number of methyl groups
at the branch ends per 1000 carbon atoms is S.C.B.

(4) Weight average molecular weight by light
scattering method

15 This item was measured at 125°C by the normal
method, with α -chloronaphthalin used as a solvent and
employing a photoelectric type light scattering photo-
meter (manufactured by SHIMAZU SEISAKUSHO).

(5) Melt index (MI)

20 According to the condition E of ASTM D 1238.

(6) Melt flow ratio (MFR)

Firstly, $MI_{21.6}$ (grams per 10 min. under a load
of 21.6 kg at 190°C) is measured according to ASTM D 1238
condition F. Then, MFR is calculated using the following
25 formula.

$$MFR = MI_{21.6}/MI$$

(7) Rigidity (expressed by Olsen's flexural modulus)
According to ASTM D 747.

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- 1 Press condition: ASTM D 1898 method C
Test piece: 25 x 70 x 1 mm thickness
Span: 25 mm
Measurement temperature: 20°C
- 5 (8) Tensile impact strength: According to ASTM D 1822
Press condition: ASTM D 1898 method C
Test piece: S type dumbbell, 1 mm thickness
Annealing: 1 hour in boiling water
Measurement temperature: 20°C
- 10 (9) Molecular weight distribution (\bar{M}_w/\bar{M}_n)
GPC method (gel permeation chromatography
method)
HLC-811 (manufactured by TOYO SODA)
Column: TSK-GEL (GMSP + G₇₀₀₀H₄ + GMHx2)
- 15 Solvent: 1,2,4-trichlorobenzene (TCB)
Temperature: 145°C
Detector: Differential refractometer
Flow quantity: 1 ml/min.
Concentration: 15 mg/10 ml TCB
- 20 Measurement data on standard polystyrenes are
shown below.

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| Polystyrene | Nominal value | | | Measured value | | |
|-------------------------|--------------------|--------------------|-----------------------|----------------|-------------|-----------------------|
| | \bar{M}_w | \bar{M}_n | \bar{M}_w/\bar{M}_n | \bar{A}_w | \bar{A}_n | \bar{A}_w/\bar{A}_n |
| #41955 (Waters') | 9.82×10^4 | 9.62×10^4 | 1.02 | 2083 | 1744 | 1.19 |
| A 5000 (TOYO SODA's) | 6.2×10^3 | 5.96×10^3 | 1.04 | 140 | 112 | 1.25 |

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- 1 (10) Environmental stress-cracking resistance (ESCR)
According to ASTM D 1693.
Expressed in F₅₀ (hr).
The following exceptions were adopted.
- 5 Concentration of Antarox-C0630: 10% by weight
Sample: 3 mm thickness, 0.5 mm notch
- (11) Tensile strength
According to ASTM D 638.
- (12) Resistance to chlorine water
Test solution: 0.2% chlorine water
Solution quantity: A quantity which gives
1.2 ml/cm² against a pressed
sample. The solution is
replaced daily.
- 10 Temperature: 40°C
Evaluation: 10 stage evaluation on a sample
after 72 hours.
1: Excellent,
10: Overall surface like "foam"
- 15 Transparency (haze value)
Press condition: 180°C x 10 min, rapid cooling
in ice water
Sample: 100μ thickness
Haze measurement: Internal haze
- 20 (13) Brabender torque
Brabender plastograph ® was used.
Jacket: W 50 model, 45 g filled
Temperature: 190°C
- 25 (14)

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1 Rotor revolution: 60 rpm
A torque after 30 min. is expressed in kg-m.

(15) Spiral flow length
Injection molding machine: 5 ounce injection

5 molding machine manufactured by the
Japan Steel Works, Ltd.

Mold: Spiral mold (7.5 mmØ semicircle, 2000 mm
length)

Molding condition: Resin temperature 250°C

10 Mold temperature 40°C

Injection pressure 840 kg/cm²

Injection molding is carried out with this mold-
ing condition and spiral flow length is measured.

15 The present invention is explained below in more
detail by the following examples, but it is not restricted
by these examples.

Example 1

(1) Synthesis of Organomagnesium Compound
20 In a 500 ml four-necked flask equipped with a
stirrer, a reflux condenser, and a dropping funnel was
placed 16.0 g of flake-shaped magnesium to be used for
the production of Grignard reagents. The air and mois-
ture inside the flask were completely replaced by
25 nitrogen. Into the dropping funnel were charged 68 ml
(0.65 mol) of n-butyl chloride and 30 ml of n-butyl
ether. About 30 ml of this solution was dropped into

1 the flask to initiate a reaction, and thereafter the rest
of the solution was dropped in 4 hours at 50°C. After
the completion of dropping, the reaction was continued
for further 1.5 hours at 60°C. Then, the reaction system
5 was cooled to room temperature and the unreacted magnesium
was filtered off by the use of a glass filter.

n-Butyl magnesium chloride in the n-butyl ether
was measured for its concentration by hydrolyzing with 1 N
sulfuric acid and back-titrating with 1 N sodium hydroxide
10 using phenolphthalein as an indicator. The concentration
was 1.96 mol/l.

(2) Synthesis of Solid Catalyst Component

The air and moisture inside a 500 ml four-necked flask equipped with a stirrer, a dropping funnel
15 and a thermometer was completely replaced by nitrogen.
In the flask was placed 130 ml of the n-butyl ether
solution containing 0.26 mol of n-butyl magnesium chloride
synthesized in the above step (1). From the dropping
funnel was dropped 30 ml (0.26 mol) of silicon tetra-
20 chloride over 2 hours at 50°C. The reaction was con-
tinued for further 1 hour at 60°C. The formed white
solid was separated, washed with n-heptane and dried
under reduced pressure to obtain 31.5 g of a white solid.

Ten grams of this white solid was placed in a 100 ml
25 four-necked flask and 50 ml of titanium tetrachloride
was added. They were allowed to react with stirring for
1 hour at 100°C. After the completion of the reaction,
n-heptan washing was applied until the washings became

1 free from titanium tetrachloride. After drying under
reduced pressure, 7.9 g of a solid catalyst component
was obtained. Each 1 g of this solid catalyst component
supported 14 mg of titanium.

5 Example 2

Ethylene- α -olefin copolymers A were polymerized,
using the catalyst produced in Example 1 and organoaluminum
compounds (co-catalyst) and employing various α -olefins
and other polymerization conditions as shown in Table 1.

10 Densities, intrinsic viscosities, S.C.B. and (weight
average molecular weight/number average molecular weight)
of these polymers obtained were also shown in Table 1.

These copolymers are used in the following
examples as mixing components.

15 Example 3

Ethylene- α -olefin copolymers B were polymerized,
using the catalyst produced in Example 1 and organoalumi-
num compounds (co-catalyst) and employing various α -olefins
and other polymerization conditions as shown in Table 2.

20 Densities, intrinsic viscosities, S.C.B. and (weight
average molecular weight/number average molecular weight)
of these ethylene- α -olefin copolymers were also shown in
Table 2.

These copolymers are used in following examples
25 as mixing components.

Table 1

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst (mmol) | Solvent (kg) | α -olefin (kg) | H ₂ partial pressure (kg/cm ²) |
|-------|-----------------------|------------------------------------|------------------------|--------------------|---------------------|------------------------|---|
| A1-1 | Slurry | 65 | 134 | TEA 100 | C ₄ 6.0 | C ₄ ' 6.14 | 0.84 |
| A1-2 | Solution | 1 | 25.3 | DEAC 2.5 | C ₇ 0.25 | 4-MP-1 0.110 | 0.1 |
| A1-3 | Slurry | 65 | 130 | TEA 50 | C ₄ 6.0 | C ₄ ' 6.14 | 0.25 |
| A1-4 | " | 65 | 310 | TEA 100 | " | " | 0.86 |
| A1-5 | " | 65 | 102 | TEA 50 | " | " | 0.059 |
| A1-6 | Solution | 1 | 26.0 | DEAC 2.5 | C ₇ 0.30 | C ₆ ' 0.060 | 0.1 |
| A1-7 | " | 1 | 327 | TEA 100 | " | " | 1.8 |
| A1-8 | " | 1 | 24.5 | DEAC 2.5 | " | 4-MP-1 0.050 | 0.15 |
| A1-9 | Slurry | 65 | 330 | TEA 100 | C ₄ 6.0 | C ₄ ' 6.14 | 1.1 |
| A1-10 | " | 65 | 309 | TEA 100 | " | " | 1.2 |
| A1-11 | " | 65 | 121 | TEA 50 | " | " | 0.98 |
| A1-12 | " | 65 | 320 | TEA 100 | " | " | 3.0 |
| A1-13 | Solution | 1 | 25.0 | DEAC 2.5 | C ₇ 0.25 | C ₈ ' 0.140 | 0.1 |

- Cont'd -

Table 1 (Cont'd)

| Properties | | | | | | Note |
|--|---|---------------------------------|-----|------------------|-----------|----------------------------------|
| C_2' - partial pressure (kg/cm ²) | Polymeriza- tion tempera- ture (°C) | Density (g/cm ³) | [η] | S.C.B. (dl/g) | M_w/M_n | |
| 5.6 | 50 | 0.900 | 2.2 | 38 | 5.9 | TEA = Triethyl aluminum |
| 20 | 140 | 0.904 | 2.5 | 23 | 3.6 | DEAC = Diethyl aluminum chloride |
| 6.0 | 50 | 0.905 | 3.2 | 30 | 5.8 | 4-MP-1: 4-Methylpentene-1 |
| 9.5 | 50 | 0.915 | 2.5 | 1.9 | 5.5 | C_2' = Ethylene |
| 4.5 | 50 | 0.908 | 4.4 | 25 | 6.0 | C_4' = n-Butane |
| 20 | 140 | 0.903 | 2.5 | 25 | 3.7 | C_4' = Butene-1 |
| 12.0 | 140 | 0.922 | 2.2 | 13 | 5.3 | C_6' = Hexene-1 |
| 20 | 140 | 0.920 | 2.5 | 10 | 3.7 | C_8' = Octene-1 |
| 12.0 | 50 | 0.921 | 2.5 | 13 | 5.5 | C_7' = n-Heptane |
| 8.0 | 50 | 0.911 | 2.2 | 25 | 5.7 | |
| 6.5 | 50 | 0.907 | 2.2 | 30 | 5.7 | |
| 20 | 50 | 0.928 | 2.2 | 8 | 5.3 | |
| 20 | 140 | 0.903 | 2.5 | 24 | 3.9 | |

Table 2

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst (mmol) | Solvent (kg) | α -olefin (kg) | H ₂ partial pressure (kg/cm ²) |
|-------|-----------------------|------------------------------------|------------------------|--------------------|---------------------|------------------------|---|
| B1-1 | Slurry | 65 | 345 | TEA 100 | C ₄ 15.2 | C ₄ ' 1.2 | 11.5 |
| B1-2 | Solution | 1 | 25.5 | DEAC 2.5 | C ₇ 0.28 | 4-MP-1 0.030 | 3.0 |
| B1-3 | Slurry | 65 | 415 | TEA 50 | C ₄ 15.2 | C ₄ ' 1.6 | 11.0 |
| B1-4 | " | 65 | 425 | " | " | C ₄ ' 2.0 | 10.5 |
| B1-5 | " | 65 | 286 | " | C ₄ 6.0 | C ₄ ' 6.14 | 9.4 |
| B1-6 | " | 65 | 410 | TEA 100 | C ₄ 12.0 | C ₄ ' 3.0 | 11.0 |
| B1-7 | Solution | 1 | 25.7 | DEAC 2.5 | C ₇ 0.25 | 4-MP-1 0.050 | 2.5 |
| B1-8 | Slurry | 65 | 250 | TEA 100 | C ₄ 15.2 | C ₄ ' 0.4 | 13.5 |
| B1-9 | " | 65 | 407 | " | " | C ₄ ' 0.5 | 13.0 |
| B1-10 | " | 65 | 422 | TEA 50 | " | C ₄ ' 1.8 | 11.0 |
| B1-11 | " | 65 | 405 | " | " | C ₄ ' 1.4 | 11.0 |
| B1-12 | Solution | 1 | 26 | DEAC 2.5 | C ₇ 0.25 | C ₈ ' 0.040 | 3.0 |

- Cont'd -

Table 2 (Cont'd)

| C_2' - pressure (kg/cm ²) | Polymeriza- tion tempera- ture (°C) | Properties | | | | Note |
|---|---|---------------------------------|---------------|--------|-----------------------|----------------------------------|
| | | Density (g/cm ³) | [η] (dl/g) | S.C.B. | \bar{M}_w/\bar{M}_n | |
| 5.0 | 70 | 0.943 | 0.63 | 15 | 5.5 | |
| 10 | 140 | 0.938 | 0.50 | 13 | 3.5 | TEA = Triethyl aluminum |
| 5.0 | 70 | 0.936 | 0.62 | 20 | 5.6 | DEAC = Diethyl aluminum chloride |
| 5.0 | 70 | 0.929 | 0.65 | 25 | 5.7 | $4-MP-1$ = 4-Methylpentene-1 |
| 8.5 | 50 | 0.927 | 1.1 | 25 | 5.8 | C_2' = Ethylene |
| 3.0 | 50 | 0.910 | 0.60 | 35 | 5.9 | C_4 = n-Butane |
| 10 | 140 | 0.912 | 0.52 | 22 | 3.6 | C_4' = Butene-1 |
| 1.5 | 50 | 0.930 | 0.28 | 25 | 5.7 | C_6' = Hexane-1 |
| 5.0 | 70 | 0.954 | 0.62 | 8 | 5.2 | C_8' = Octene-1 |
| 5.0 | 70 | 0.934 | 0.61 | 22 | 5.6 | C_7 = n-Heptane |
| 5.0 | 70 | 0.939 | 0.62 | 18 | 5.5 | |
| 10 | 140 | 0.937 | 0.49 | 14 | 3.6 | |

1 Example 4

Ethylene- α -olefin copolymers A were polymerized, using the catalyst produced in Example 1 and organo-aluminum compounds (co-catalyst) and employing various 5 α -olefins and other polymerization conditions shown in Table 3. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these ethylene/ α -olefin copolymers were also shown in Table 3.

10 These copolymers are used in the following examples as mixing components.

Example 5

Ethylene- α -olefin copolymers B were polymerized, using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing various α -olefins and other polymerization conditions as shown in 15 Table 4. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these ethylene/ α -olefin copolymers were also 20 shown in Table 4.

These copolymers are used in the following examples as mixing components.

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Table 3

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst (mmol) | Solvent (kg) | α -olefin (kg) | H ₂ partial pressure (kg/cm ²) |
|-------|-----------------------|------------------------------------|------------------------|--------------------|---------------------|------------------------|---|
| A2-1 | Slurry | 65 | 145 | TEA 100 | C ₄ 6.0 | C ₄ ' 6.14 | 1.38 |
| A2-2 | Solution | 1 | 25.5 | DEAC 2.5 | C ₇ 0.25 | 4-MP-1 0.11 | 0.5 |
| A2-3 | Slurry | 65 | 141 | TEA 50 | C ₄ 6.0 | C ₄ ' 6.14 | 0.59 |
| A2-4 | " | 65 | 307 | TEA 100 | " | " | 2.3 |
| A2-5 | " | 65 | 311 | " | " | " | 1.84 |
| A2-6 | " | 65 | 321 | " | " | " | 3.2 |
| A2-7 | Solution | 1 | 26.5 | DEAC 2.5 | C ₇ 0.3 | 4-MP-1 0.05 | 0.9 |
| A2-8 | Slurry | 65 | 315 | TEA 100 | C ₄ 6.0 | C ₄ ' 6.14 | 2.6 |
| A2-9 | " | 65 | 118 | " | " | " | 4.6 |
| A2-10 | Solution | 1 | 24.5 | DEAC 2.5 | C ₇ 0.3 | C ₆ ' 0.025 | 0.9 |

- Cont'd -

Table 3 (Cont'd)

| C_2' - partial pressure (kg/cm ²) | Polymer- ization temperature (°C) | Properties | | | | Note |
|--|--|---------------------------------|---------------|--------|-----------------------|----------------------------------|
| | | Density (g/cm ³) | [η] (dl/g) | S.C.B. | \bar{M}_w/\bar{M}_n | |
| 6.0 | 50 | 0.902 | 1.8 | 38 | 5.9 | TEA = Triethyl aluminum |
| 20 | 140 | 0.908 | 1.8 | 23 | 3.8 | DEAC = Diethyl aluminum chloride |
| 6.5 | 50 | 0.907 | 2.5 | 30 | 5.8 | 4-MP-1 = 4-Methylpentene-1 |
| 11 | 50 | 0.918 | 1.8 | 17 | 5.4 | C_2' = Ethylene |
| 8.4 | 50 | 0.914 | 1.8 | 25 | 5.7 | C_4 = n-Butane |
| 14 | 50 | 0.925 | 1.8 | 13 | 5.3 | C_4' = Butene-1 |
| 20 | 140 | 0.923 | 1.8 | 10 | 3.6 | C_6' = Hexene-1 |
| 8.5 | 50 | 0.914 | 1.6 | 25 | 5.5 | C_7 = n-Heptane |
| 17 | 50 | 0.929 | 1.6 | 10 | 5.3 | |
| 20 | 140 | 0.918 | 1.8 | 13 | 3.8 | |

Table 4

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst (mmol) | Solvent (kg) | α -olefin (kg) | H_2 partial pressure (kg/cm^2) |
|------|-----------------------|------------------------------------|------------------------|--------------------|--------------|-----------------------|--------------------------------------|
| B2-1 | Slurry | 65 | 348 | TEA 100 | C_4 15.2 | C_4' 1.0 | 12 |
| B2-2 | Solution | 1 | 26.5 | DEAC 2.5 | C_7 0.28 | 4-MP-1 0.03 | 3.0 |
| B2-3 | Slurry | 65 | 405 | TEA 50 | C_4 15.2 | C_4' 1.6 | 8.8 |
| B2-4 | " | 65 | 421 | " | " | " | 12 |
| B2-5 | " | 65 | 407 | TEA 100 | C_4 12.0 | C_4' 2.5 | 12 |
| B2-6 | Solution | 1 | 25.7 | DEAC 2.5 | C_7 0.25 | 4-MP-1 0.05 | 2.5 |
| B2-7 | Slurry | 65 | 245 | " | C_4 15.2 | C_4' 0.3 | 12 |
| B2-8 | " | 65 | 420 | TEA 50 | " | C_4' 1.2 | 12 |
| B2-9 | Solution | 1 | 23.9 | DEAC 2.5 | C_7 0.30 | C_6' 0.017 | 3.0 |

- Cont'd -

Table 4 (Cont'd)

| C_2' - partial pressure (kg/cm ²) | Polymeri- zation tempera- ture (°C) | Properties | | | | |
|--|---|---------------------------------|----------------------|--------|-----------|----------------------------------|
| | | Density (g/cm ³) | [η] (dl/g) | S.C.B. | M_w/M_n | Note |
| 3.0 | 70 | 0.943 | 0.51 | 15 | 5.9 | TEA = Triethyl aluminum |
| 10 | 140 | 0.938 | 0.50 | 13 | 3.5 | DEAC = Diethyl aluminum chloride |
| 5.0 | 70 | 0.935 | 0.73 | 20 | 5.9 | 4-MP-1 = 4-methylpentene-1 |
| 3.0 | 70 | 0.929 | 0.54 | 25 | 5.9 | C_2' = Ethylene |
| 3.0 | 50 | 0.910 | 0.51 | 35 | 6.0 | C_4 = n-Butane |
| 10 | 140 | 0.912 | 0.52 | 22 | 3.6 | C_4' = Butene-1 |
| 1.0 | 50 | 0.931 | 0.25 | 25 | 5.9 | C_6' = Hexene-1 |
| 3.0 | 70 | 0.938 | 0.50 | 18 | 5.4 | C_7 = n-Heptane |
| 10 | 140 | 0.937 | 0.52 | 18 | 3.4 | |

1 Example 6

A composition of ethylene- α -olefin copolymers was prepared in two stage polymerization.

The first stage polymerization was carried out 5 for 90 min. by using the catalyst produced in Example 1 and triethyl aluminum (co-catalyst) and employing other polymerization conditions as shown in Table 5. Successively, the second stage polymerization was conducted for 123 min. by changing only the hydrogen 10 partial pressure and the ethylene partial pressure as shown in Table 5. In both polymerization stages, the liquid phase molar ratio of ethylene/butene-1/hydrogen was maintained at respective fixed levels. The polymerized quantities in each stage were examined from the 15 quantities of fed ethylene. The result indicated that the total polymer consisted of about 45% by weight of higher molecular weight components and about 55% by weight of lower molecular weight components. The sample polymer of the former stage was taken out immediately 20 before the completion of the polymerization and was measured for its density, intrinsic viscosity, S.C.B. and (weight average molecular weight/number average molecular weight). Also, similar measurements were made 25 for the whole polymer obtained after the two-stage polymerization. Using the values of the former stage polymer and the whole polymer, the intrinsic viscosity and S.C.B. for the polymer formed in the latter stage alone were calculated. These calculated values are also shown in

1 Table 5. The whole polymer gave: density 0.920 g/cm³, melt index 0.7 g/10 min, melt flow ratio 65, intrinsic viscosity 1.6 dl/g, S.C.B. 25. The whole polymer was measured for its fluidity and solid physical properties.

5 Results are shown in Table 9.

The below-described are mixing methods of an ethylene- α -olefin copolymer A having a relatively higher molecular weight and an ethylene- α -olefin copolymer B having a relatively lower molecular weight.

10 (a) Mixing with a Banbury mixer (hereinafter referred to as Banbury mixing)

A copolymer A and a copolymer B are mixed in a fixed ratio and in order to give a total quantity of 1.0 kg. The mixture is kneaded in a Banbury mixer for 5 min.

15 with a rotar revolution of 150 to 230 rpm. At that time, nitrogen replacement should be made sufficiently and the polymer temperature must not exceed 250°C.

(b) Mixing in a solution state (hereinafter referred to as solution mixing)

20 A copolymer A and a copolymer B are mixed in a fixed ratio and in order to give a total quantity of 100 g. This mixture is charged into a 3 liter autoclave. Two liters of xylene is added as a solvent. With stirring, the mixture is heated up to 200°C and is subjected to

25 1 hour of solution mixing. Then, it is cooled below the boiling point, and is added into 10 liters of methanol to cause precipitation. The precipitate is dried for 48 hours in a vacuum drier of 80°C to obtain an intended.

1 polymer composition.

Example 7

A composition of ethylene- α -olefin copolymers was prepared in two stage polymerization.

5 The first stage polymerization was carried out for 100 min. by using the catalyst produced in Example 1 and triethyl aluminum (co-catalyst) and employing other polymerization conditions as shown in Table 6. Successively the second stage polymerization was conducted for
10 150 min. by changing only the hydrogen partial pressure and the ethylene partial pressure as shown in Table 6. In both polymerization stages, the liquid phase molar ratio of ethylene/butene-1/hydrogen was maintained at respective fixed levels. The polymerized quantitites
15 in each stage were examined from the quantities of fed ethylene. The result indicated that the total polymer consisted of about 50% by weight of higher molecular weight components and about 50% by weight of lower molecular weight components. The sample polymer of the
20 former stage was taken out immediately before the completion of the polymerization and was measured for its density, intrinsic viscosity, S.C.B. and (weight average molecular weight / number average molecular weight). Similar measurements were made also for the whole polymer
25 obtained after the two stage polymerization. Using the values of the former stage polymer and the whole polymer, the intrinsic viscosity and S.C.B. for the polymer formed

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1 in the latter stage alone were calculated. These-cal-
culated values are also shown in Table 6. The whole
polymer gave: density 0.923 g/cm^3 , melt index 6 g/10 min.,
melt flow ratio 55, intrinsic viscosity 1.10 dl/g, S.C.B.
5 25. The whole polymer was subjected to injection molding
and the molded composition was measured for its physical
properties. Results are shown in Table 10.

Table 5

| No. | Polymerization method | Polymerization vessel capacity (λ) | Catalyst quantity (mg) | Co-catalyst TEA (mg) | Solvent (g) | α -olefin (g) | H ₂ partial pressure (kg/cm ²) |
|-----------|-----------------------|--|------------------------|----------------------|-------------|----------------------|---|
| 1st stage | Slurry | 5 | 18.5 | 5 | C_4 1000 | C_4' 250 | 0.3 |
| 2nd stage | Slurry | | | | | | 1.7 |

- Cont'd -

Note C_4 = n-Butane C_4' = Butene-1 C_2' = Ethylene

TEA = Triethyl aluminum

Values in parenthesis are calculated values.

Table 5 (Cont'd)

| C_2' - partial pressure (kg/cm ²) | Polymeri- zation tempera- ture (°C) | Polymeri- zation time (min) | Properties | | | |
|--|---|--------------------------------------|---------------------------------|---------------|--------|-----------------------|
| | | | Density (g/cm ³) | [η] (dl/g) | S.C.B. | \bar{M}_w/\bar{M}_n |
| 3 | 50 | 90 | 0.902 | 2.8 | 35 | 6.1 |
| 8 | | 123 | - | (0.62) | (15) | - |

Table 6

| No. | Polymerization method | Polymerization vessel capacity (λ) | Catalyst quantity (mg) | Co-catalyst TEA (mmol) | Solvent (g) | α -olefin (g) | H ₂ partial pressure (kg/cm ²) |
|-----------|-----------------------|--|------------------------|------------------------|-------------|----------------------|---|
| 1st stage | Slurry | | 25 | 5 | C_4 1000 | C_4' 120 | 0.45 |
| 2nd stage | Slurry | | | | | | 16 |

Note C_4 = n-Butane
 C_4' = Butene-1
 C_2' = Ethylene

TEA = Triethyl aluminum

Values in parenthesis are calculated values.

- Cont'd -

Table 6 (Cont'd)

| C_2' - partial pressure (kg/cm ²) | Polymeri- zation tempera- ture (°C) | Polymeri- zation time (min) | Properties | | | |
|--|---|--------------------------------------|---------------------------------|--------------------|--------|-----------------------|
| | | | Density (g/cm ³) | $[\eta]$ (dl/g) | S.C.B. | \bar{M}_w/\bar{M}_n |
| 20 | 50 | 100 | 0.910 | 1.75 | 30 | 5.8 |
| | | 150 | - | (0.5) | (20) | - |
| 4.0 | | | | | | |

1 Example 8

The ethylene- α -olefin copolymer Al-1 obtained in Example 2 and the ethylene- α -olefin copolymer Bl-1 obtained in Example 3 were mixed at a 50/50 weight ratio 5 and kneaded in a Banbury mixer. A composition having a density, MI and MFR shown in Table 7 was prepared. Physical properties of the composition were also shown in Table 7. For the purpose of comparison, in Table 7 were also shown Comparative example 1 using a high pressure 10 polyethylene based on the conventional technique (commercial product: Sumikathene ^(R) F101-1 manufactured by Sumitomo Chemical Co., Ltd.) as well as Comparative example 2 using a low density ethylene- α -olefin copolymer of the conventional technique.

15 As is obvious from Table 7, the polymer composition of this invention is excellent, compared with the high pressure polyethylene, with its lower Brabender torque (excellent in processability) and higher tensile impact strength, ESCR, rigidity and tensile strength.

20 It is also obvious from Table 7 that, compared with the low density ethylene- α -olefin copolymer of the conventional technique, the polymer composition of this invention has a much lower Brabender torque (very excellent in processability) and a much higher tensile impact 25 strength and tensile strength.

Table 7

| Mixing method | Copolymer A | | Copolymer B | | | | Properties of composition | | |
|-----------------------|-------------|-------------|-------------|-------------|------------------------------|---------------|---------------------------|-------------------------------|-----|
| | Designation | % by weight | Designation | % by weight | Density (g/cm ³) | MI (g/10 min) | MFR | Distribution index of S.C.B.* | |
| Example 8 | Banbury | A1-1 | 5.0 | B1-1 | 50 | 0.921 | 1.1 | 65 | 2.5 |
| Comparative Example 1 | - | - | - | - | 0.922 | 0.3 | 65 | - | - |
| Comparative Example 2 | - | - | - | - | 0.920 | 1.0 | 30 | - | - |

- Cont'd -

* Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

Table 7 (Cont'd.)

| Physical properties of composition | | | | | |
|--|--|---------------|--|-------------------------|---------------------------|
| Tensile impact strength (kg-cm/cm ²) | Olsen's flexural modulus (kg/cm ²) | ESCR F50 (hr) | Tensile strength (kg/cm ²) | Brabender torque (kg.m) | Chlorine water resistance |
| 340 | 2600 | 1000 | 290 | 1.9 | 1 |
| 200 | 2200 | 30 | 180 | 2.2 | 5 |
| 230 | 3200 | 1000 | 250 | 2.9 | 2 |

1 Example 9

The ethylene- α -olefin copolymer A2-1 obtained in Example 4 and the ethylene- α -olefin copolymer B2-1 obtained in Example 5 were mixed at a 50/50 weight ratio 5 and kneaded in a Banbury mixer. A composition having a density, melt index and melt flow ratio shown in Table 8 was prepared. Physical properties of the composition were also shown in Table 8. For the purpose of comparison, in Table 8 were also shown Comparative example 3 10 using a high pressure method polyethylene based on the conventional technique (commercial product: Sumikathene^{RG} 701 manufactured by Sumitomo Chemical Co., Ltd.) as well as Comparative example 4 using a low density ethylene- α -olefin copolymer of the conventional technique. As is 15 obvious from Table 8, the polymer composition of this invention has a better fluidity at injection molding than the high pressure polyethylene and, moreover, has a much higher tensile impact strength, rigidity, ESCR and tensile strength. Also, the polymer composition of the 20 present invention is largely excellent in fluidity at injection molding, compared with the low density ethylene- α -olefin copolymer of the conventional technique, and further has a much higher tensile impact strength and ESCR.

25 Examples 10 to 14

Ethylene- α -olefin copolymers A obtained in Example 2 and ethylene- α -olefin copolymers B obtained in

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1 Example 3 were mixed in various ratios and the compositions having densities, MIs and MFRs shown in Table 9 were obtained. Their physical properties were also shown in Table 9.

5 In Table 9 was also shown a similar composition obtained from two stage polymerization (Example 6). For the purpose of comparison, in Table 9 were also shown Comparative examples 5, 6 and 7 as examples of low density ethylene- α -olefin copolymers of the conventional technique
10 of which molecular weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.

As is obvious from Table 9, in the compositions of this invention, S.C.B. in higher molecular weight components is more than or about equal to that in lower molecular weight components as seen in distribution index of S.C.B. (compare Examples 6, 10 and 14 with Comparative examples 5 and 6, and Example 13 with Comparative example 7). Therefore, the compositions of this invention have much higher tensile impact strengths and tensile strengths than the comparative compositions of the conventional technique do. By comparison of Comparative example 2 in Table 7 with Comparative example 5 in Table 9, it is seen that widening of molecular weight distribution in the manufacture of a low density ethylene- α -olefin copolymer of the conventional technique maintaining density and MI (larger MFR gives wider distribution)

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- 1 results in large reduction in tensile impact strength
and tensile strength.

Table 8

| | Mixing method | Copolymer A | | Copolymer B | | Properties of composition | | |
|-----------------------|---------------|--------------------|-------------|-------------|-------------|------------------------------|---------------|-----|
| | | Design-% by weight | % by weight | Designation | % by weight | Density (g/cm ³) | MI (g/10 min) | MFR |
| Example 9 | Banbury | A2-1 | 50 | B2-1 | 50 | 0.924 | 5 | 50 |
| Comparative Example 3 | - | - | - | - | - | 0.920 | 6 | 35 |
| Comparative Example 4 | - | - | - | - | - | 0.924 | 5 | 30 |

- Cont'd -

* Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

Table 8 (Cont'd)

| Tensile impact strength (kg-cm/cm ²) | Olsen's flexural modulus (kg/cm ²) | ESCR F ₅₀ (hr) | Tensile strength (kg/cm ²) | Spinal blow length (mm) |
|---|---|------------------------------|---|----------------------------|
| 190 | 2900 | 100 | 220 | 130 |
| 120 | 2100 | 2 | 150 | 120 |
| 110 | 3500 | 30 | 180 | 80 |

Table 9

| | Mixing method | Copolymer A | | Copolymer B | | Properties of composition | | |
|---|---------------|-------------|-------------|-------------|-------------|------------------------------|---------------|-----|
| | | Designation | % by weight | Designation | % by weight | Density (g/cm ³) | MI (g/10 min) | MFR |
| Example 6 - Two stage polymerization - | | | | | | | | |
| Example 10 | Solution | A1-2 | 60 | B1-2 | 40 | 0.920 | 0.5 | 70 |
| Example 11 | Banbury | A1-3 | 50 | B1-3 | 50 | 0.920 | 0.25 | 80 |
| Example 12 | " | A1-4 | 50 | B1-4 | 50 | 0.920 | 0.8 | 50 |
| Example 13 | " | A1-11 | 50 | B1-9 | 50 | 0.929 | 1.2 | 70 |
| Example 14 | Solution | A1-13 | 60 | B1-12 | 40 | 0.919 | 0.5 | 70 |
| Comparative Example 5 | Banbury | A1-7 | 50 | B1-6 | 50 | 0.920 | 1.1 | 65 |
| Comparative Example 6 | Solution | A1-8 | 60 | B1-7 | 40 | 0.919 | 0.5 | 70 |
| Comparative Example 7 | Banbury | A1-12 | 50 | B1-10 | 50 | 0.930 | 1.2 | 70 |

- Cont'd -

(S.C.B. of copolymer A)
* Distribution index = $\frac{(S.C.B. \text{ of copolymer A})}{(S.C.B. \text{ of copolymer B})}$

Table 9 (Cont'd)

Physical properties of composition

| Tensile impact strength (kg-cm/cm ²) | Olsen's flexural modulus (kg/cm ²) | Tensile strength (kg/cm ²) | Tackiness |
|--|--|--|-----------|
| 370 | 2700 | 300 | o |
| 480 | 2600 | 320 | o |
| 480 | 2700 | 320 | o |
| 300 | 2900 | 260 | o |
| 250 | 3700 | 250 | o |
| 500 | 2500 | 310 | o |
| 110 | 3200 | 180 | x |
| 200 | 3100 | 200 | x |
| 70 | 4500 | 200 | o |

1 Examples 15 to 17

Ethylene- α -olefin copolymers A obtained in Example 4 and ethylene- α -olefin copolymers B obtained in Example 5 were mixed in various ratios and the compositions having densities, melt indices and melt flow ratios shown in Table 10 were obtained. Their physical properties were also shown in Table 10.

In Table 10 was also shown a similar composition obtained from two stage polymerization (Example 7).

- 10 For the purpose of comparison, in Table 10 were also shown Comparative examples 8, 9 and 10 as examples of low density ethylene- α -olefin copolymers of the conventional technique of which molecular weight distributions are made wider, and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.

As is obvious from Table 10, in the compositions of this invention, the higher molecular weight components have larger S.C.B. than the lower molecular weight components do, as seen in distribution index of S.C.B. (compare Examples 7, 15, 16 with Comparative examples 8 and 9, and Example 17 with Comparative example 10). Therefore, the compositions of this invention have much higher tensile impact strengths ESCRs and tensile strengths than the comparative compositions of the conventional technique do. By comparison of Comparative example 4 in Table 8 with Comparative example 9 in Table 10, it is seen that widening of molecular weight

1 distribution in the manufacture of a low density ethylene-
α-olefin copolymer of the conventional technique maintaining density and MI (larger MFR gives wider distribution)
results in large reduction in tensile impact strength,
5 ESCR and tensile strength.

Examples 18 to 20

Ethylene-α-olefin copolymers A obtained in Example 2 and ethylene-α-olefin copolymers B obtained in Exmaple 3 were mixed in various ratios and the compositions having densities, MIs and MFRs shown in Table 11 were obtained. Their physical properties were also shown in Table 11.

For the purpose of comparison, in Table 11 were also shown an example (Comparative example 1) of 15 high pressure polyethylenes of the conventional technique; an example (Comparative example 11) of low density ethylene-α-olefin copolymers of the conventional technique of which molecular weight distributions are made wider, and of which lower molecular weight components 20 have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.; and an example (Comparative example 12, to be compared with Example 19) of ethylene-α-olefin copolymers compositions of which 25 distribution indices of S.C.B. meet the object of this invention but of which lower molecular weight components have a too low intrinsic viscosity.

It is clearly seen from Table 11 that proper

1 selection of distribution index of S.C.B. gives good
transparency about equal to that of high pressure poly-
ethylenes as well as a much more excellent tensile impact
strength and tensile strength than those of high pressure
5 polyethylenes.

It is learned from comparison of Example 19
with Comparative example 12 that a too low intrinsic
viscosity of lower molecular weight components badly
affects the tensile impact strength and transparency of
10 the copolymer composition.

Table 10

| | Mixing method | Copolymer A | | Copolymer B | | Properties of composition | | |
|---|---------------|-------------|-------------|-------------|-------------|------------------------------|---------------|----------|
| | | Designation | % by weight | Designation | % by weight | Density (g/cm ³) | MI (g/10 min) | MFR |
| Example 7 - Two stage polymerization - | | | | | | | | |
| Example 15 | Solution | A2-2 | 50 | B2-2 | 50 | 0.923 | 6 | 55 (1.5) |
| Example 16 | " | A2-3 | 30 | B2-3 | 70 | 0.924 | 3 | 60 1.5 |
| Example 17 | Banbury | A2-8 | 45 | B2-8 | 55 | 0.929 | 10 | 45 1.4 |
| Comparative Example 8 | Solution | A2-7 | 50 | B2-6 | 50 | 0.922 | 5 | 50 0.45 |
| Comparative Example 9 | Banbury | A2-4 | 50 | B2-5 | 50 | 0.920 | 5 | 50 0.49 |
| Comparative Example 10 | " | A2-9 | 45 | B2-4 | 55 | 0.930 | 10 | 45 0.40 |

- Cont'd -

$$\text{Distribution index} = \frac{(\text{S.C.B. of copolymer A})}{(\text{S.C.B. of copolymer B})}$$

Table 10 (Cont'd)
 Physical properties of composition

| Tensile impact strength (kg-cm/cm ²) | Olsen's flexural modulus (kg/cm ²) | ESCR F ₅₀ (hr) | Tensile strength (kg/cm ²) | Tackiness |
|--|--|---------------------------|--|-----------|
| 170 | 3000 | 50 | 220 | o |
| 240 | 3000 | 100 | 250 | o |
| 190 | 3000 | 30 | 230 | o |
| 120 | 4000 | 5 | 200 | o |
| 100 | 3600 | 15 | 150 | x |
| 80 | 3200 | 13 | 130 | x |
| 40 | 4500 | 1 | 110 | o |

Table 11

| Mixing method | Copolymer A | | Copolymer B | | Properties of composition | | | | |
|------------------------|-------------|-------------|-------------|-------------|------------------------------|---------------|-----|-------------------------------|-----|
| | Designation | % by weight | Designation | % by weight | Density (g/cm ³) | MI (g/10 min) | MFR | Distribution index of S.C.B.* | |
| Example 18 Solution | A1-5 | 30 | B1-5 | 70 | 0.920 | 0.15 | 100 | 1.0 | |
| Example 19 " | A1-6 | 50 | B1-11 | 50 | 0.920 | 0.8 | 50 | 1.0 | |
| Example 20 Banbury | A1-1 | 50 | B1-4 | 50 | 0.916 | 1.1 | 65 | 1.6 | |
| Comparative Example 1 | - | - | - | - | 0.922 | 0.3 | 65 | - | |
| Comparative Example 11 | Banbury | A1-9 | 50 | B1-6 | 50 | 0.920 | 0.8 | 50 | 0.4 |
| Comparative Example 12 | " | A1-10 | 65 | B1-8 | 35 | 0.920 | 0.8 | 50 | 1.0 |

*Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

- Cont'd -

Table 11 (Cont'd)
 Physical properties of composition

| Tensile impact strength (kg-cm/cm ²) | Olsen's flexural modulus (kg/cm ²) | Tensile strength (kg/cm ²) | Tackiness | Haze (%) |
|--|--|--|-----------|----------|
| 480 | 2800 | 320 | 0 | 5 |
| 400 | 2800 | 250 | 0 | 5 |
| 420 | 2100 | 250 | 0 | 5 |
| 200 | 2200 | 180 | 0 | 5 |
| 150 | 3300 | 200 | x | 12 |
| 130 | 2800 | 220 | 0 | 15 |

1 Examples 21, 22, 23

Ethylene- α -olefin copolymers A obtained in Example 4 and ethylene- α -olefin copolymers B obtained in Example 5 were mixed at various ratios, and the compositions having densities, MIs and MFRs shown in Table 12 were obtained. Their physical properties were also shown in Table 12. For the purpose of comparison, in Table 12 were also shown Comparative example 3 using a high pressure polyethylene of the conventional technique; Comparative example 13 using a composition of low density ethylene- α -olefin copolymers of the conventional technique of which molecular weight distribution is made wider and of which lower molecular weight components have more S.C.B. and of which higher molecular weight components have less S.C.B.; and Comparative example 14 (to be compared with Example 22) using a composition of ethylene- α -olefin copolymers of which distribution index of S.C.B. meets the scope of the present invention but of which lower molecular weight components have a too low intrinsic viscosity. It is obvious from Table 12 that proper selection of distribution index of S.C.B. gives good transparency about equal to that of high pressure polyethylenes and much more excellent tensile impact strength, tensile strength and ESCR than those of high pressure polyethylenes. From comparison of Example 22 with Comparative example 14, it is learned that a too low intrinsic viscosity of lower molecular weight components badly affects tensile impact strength and transparency.

Table 12

| Mixing method | Copolymer A | | Copolymer B | | Properties of composition | | | |
|------------------------|-------------|-------------|-------------|-------------|------------------------------|---------------|-----|-------------------------------|
| | Designation | % by weight | Designation | % by weight | Density (g/cm ³) | MI (g/10 min) | MFR | Distribution index of S.C.B.* |
| Example 21 Solution | A2-10 | 50 | B2-9 | 50 | 0.923 | 5 | 50 | 0.72 |
| Example 22 Banbury | A2-5 | 50 | B2-4 | 50 | 0.922 | 5 | 50 | 1.0 |
| Example 23 " | A2-1 | 50 | B2-4 | 50 | 0.920 | 5 | 50 | 1.6 |
| Comparative Example 13 | " | A2-6 | 50 | B2-5 | 50 | 0.923 | 5 | 0.37 |
| Comparative Example 14 | " | A2-8 | 65 | B2-7 | 35 | 0.922 | 5 | 50 1.0 |
| Comparative Example 3 | - | - | - | - | 0.920 | 6 | 35 | - |

- Cont'd -

Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

Table 12 (Cont'd)

| Physical properties of composition | | | | | |
|---|---|------------------|---|-------------|----------|
| Tensile impact strength (kg-cm/cm ²) | Olsen's flexural modulus (kg/cm ²) | ESCR F50 (hr) | Tensile strength (kg/cm ²) | Tacki- ness | Haze (%) |
| 200 | 3100 | 20 | 250 | 0 | 7 |
| 170 | 2900 | 30 | 220 | 0 | 7 |
| 260 | 2500 | 200 | 230 | 0 | 7 |
| 50 | 3600 | 10 | 130 | x | 12 |
| 80 | 3200 | 30 | 190 | 0 | 12 |
| 120 | 2100 | 2 | 150 | 0 | 7 |

-1 Comparative Example 1

A commercial high pressure polyethylene (Sumikathene[®] F101-1 manufactured by Sumitomo Chemical Co., Ltd.) was measured for its physical properties and 5 subjected to blow molding.

Results were shown in Table 7 and 11.

Comparative Example 2

An ethylene- α -olefin copolymer of the conventional technique was synthesized employing polymerization 10 conditions as shown in Table 13 in which the catalyst prepared in Example 1 and triethyl aluminum (co-catalyst) were used. The copolymer gave: density 0.920 g/cm³, MI 1.0 g/10 min., MFR 30. Its physical properties were shown in Table 7.

Table 13

| Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst TEA (mmol) | Solvent (kg) | α -olefin (kg) | H_2 partial pressure (kg/cm^2) | C_2' partial pressure (kg/cm^2) | Polymerization temperature ($^{\circ}C$) | Polymerization time (min) |
|-----------------------|------------------------------------|------------------------|------------------------|--------------|-----------------------|--------------------------------------|---------------------------------------|--|---------------------------|
| Slurry | 65 | 197 | 100 | C_4 7.0 | C_4' 7.16 | 4.2 | 10 | 50 | 100 |

Note TEA = Triethyl aluminum

C_4 = n-Butane

C_2' = Ethylene

C_4' = Butene-1

1 Comparative Example 3

A commercial high pressure polyethylene (Sumikathene[®] G701 manufactured by Sumitomo Chemical Co., Ltd.) was measured for its physical properties and sub-
5 jected to injection molding.

Results were shown in Table 8 and 12.

Comparative Example 4

A low density ethylene- α -olefin copolymer of the conventional technique was synthesized employing polymerization conditions shown in Table 1⁴ in which the
10 catalyst prepared in Example 1 and triethyl aluminum (co-catalyst) were used. The copolymer gave: density 0.924 g/cm³, melt index 5 g/10 min., melt flow ratio 30. Its physical properties were shown in Table 8.

Table 14

| Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst TEA (mmol) | Solvent (kg) | α -olefin (kg) | H_2 partial pressure (kg/cm ²) | C_2' partial pressure (kg/cm ²) | Polymerization temperature (°C) | Polymerization time (min) |
|-----------------------|------------------------------------|------------------------|------------------------|--------------|-----------------------|--|---|---------------------------------|---------------------------|
| Slurry | 65 | 199 | 25 | 6.0 | C_4' 6.14 | 10.2 | 11.3 | 50 | 90 |

Note: TEA = Triethyl aluminum

 C_2' = Ethylene C_4 = n-Butane C_4' = Butene-1

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1 Comparative Examples 5, 6, 7 and 11

Compositions of ethylene- α -olefin copolymers of the conventional technique were prepared by blending ethylene- α -olefin copolymers A obtained in Example 2 and 5 ethylene- α -olefin copolymers B obtained in Example 3 at ratios shown in Table 9 or 11. However in these copolymer compositions, molecular weight distributions are made wider and lower molecular weight components have larger S.C.B. and higher molecular weight components have 10 smaller S.C.B. Densities, MIs, MFRs and physical properties of these compositions were shown in Table 9 or 11.

Comparative Example 12

By blending an ethylene- α -olefin copolymer A obtained in Example 2 and an ethylene- α -olefin copolymer 15 B obtained in Example 3 at a mixing ratio shown in Table 11, a composition of ethylene- α -olefin copolymers was prepared of which distribution index of S.C.B. meets the scope of the present invention but of which lower molecular weight components have a too low intrinsic viscosity. Its density, MI, MFR and physical properties were 20 shown in Table 11.

Comparative Examples 8, 9, 10 and 13

Compositions of ethylene- α -olefin copolymers of the conventional technique were prepared by blending 25 ethylene- α -olefin copolymers A obtained in Example 4 and ethylene- α -olefin copolymers B obtained in Example 5 at

1 mixing ratios shown in Table 10 or 12. However in these
compositions, molecular weight distributions are made
wider and lower molecular weight components have larger
S.C.B. and higher molecular weight components have smaller
5 S.C.B. Densities, MIs, MFRs and physical properties of
these compositions were shown in Table 10 or 12.

Comparative Example 1⁴

By blending an ethylene- α -olefin copolymer A obtained in Example 4 and an ethylene- α -olefin copolymer B obtained in Example 5 at a mixing ratio shown in Table 10 12, a composition of ethylene- α -olefin copolymers was prepared of which distribution index of S.C.B. meets the scope of this invention but of which lower molecular weight components have too low an intrinsic viscosity. Its density, MI, MFR and physical properties were shown 15 in Table 12.

Example 2⁴

Ethylene- α -olefin copolymers A were polymerized using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing α -olefins and other polymerization conditions as shown in Table 15. 20 Their densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) were shown in Table 15.

These polymers are used in the following examples as mixing components.

Table 15

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst (mmol) | Solvent (kg) | α -olefin (kg) | H ₂ partial pressure (kg/cm ²) |
|------|-----------------------|------------------------------------|------------------------|--------------------|---------------------|------------------------|---|
| A3-1 | Slurry | 65 | 131 | TEA 100 | C ₄ 6.0 | C ₄ ' 6.14 | 0.45 |
| A3-2 | Solution | 1 | 25.1 | DEAC 2.5 | C ₇ 0.22 | 4-MP-1 0.130 | 0.10 |
| A3-3 | " | 1 | 24.8 | " | C ₇ 0.30 | C ₆ ' 0.055 | 0.10 |
| A3-4 | Slurry | 65 | 307 | TEA 100 | C ₄ 6.0 | C ₄ ' 6.14 | 0.9 |
| A3-5 | " | 65 | 130 | TEA 50 | " | " | 0.22 |
| A3-6 | " | 65 | 125 | " | " | " | 1.8 |
| A3-7 | " | 65 | 301 | TEA 100 | " | " | 1.2 |
| A3-8 | " | 65 | 318 | " | " | " | 2.0 |
| A3-9 | " | 65 | 308 | " | " | " | 1.4 |

Note TEA = triethyl aluminum

DEAC = Diethyl aluminum chloride

- Cont'd -

4-MP-1 = 4-Methylpentene-1

C₂' = EthyleneC₄ = n-ButaneC₄' = Butene-1C₆' = Hexene-1C₇ = n-Heptane

Table 15 (Cont'd)

| C ₂ '- partial pressure (kg/cm ²) | Polymeriza- tion tempera- ture (°C) | Properties | | | |
|---|---|---------------------------------|---------------|--------|--------------------------------|
| | | Density (g/cm ³) | [η] (dl/g) | S.C.B. | M _w /M _n |
| 5.0 | 50 | 0.899 | 2.6 | 38 | 5.9 |
| 20 | 140 | 0.899 | 2.6 | 27 | 3.5 |
| 20 | 140 | 0.902 | 2.6 | 24 | 3.7 |
| 9.0 | 50 | 0.914 | 2.4 | 22 | 6.0 |
| 5.5 | 50 | 0.906 | 3.2 | 28 | 5.8 |
| 18 | 50 | 0.923 | 2.6 | 9 | 5.5 |
| 12 | 50 | 0.919 | 2.4 | 16 | 5.8 |
| 20 | 50 | 0.928 | 2.4 | 8 | 5.4 |
| 9.0 | 50 | 0.914 | 2.2 | 22 | 5.7 |

1 Example 25

Ethylene- α -olefin copolymers B were polymerized using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing α -olefins and 5 other polymerization conditions shown in Table 16. Their densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) were shown in Table 16.

These copolymers are used in the following 10 examples as mixing components.

Table 16

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst (mmol) | Solvent (kg) | α -olefin (kg) | H_2 partial pressure (kg/cm^2) |
|------|-----------------------|------------------------------------|------------------------|--------------------|---------------------|------------------------|--------------------------------------|
| B3-1 | Slurry | 65 | 405 | TEA 50 | C ₄ 12.0 | C ₄ ' 2.0 | 10.8 |
| B3-2 | Solution | 1 | 25.5 | DEAC 2.5 | C ₇ 0.30 | 4-MP-1 0.025 | 2.4 |
| B3-3 | " | 1 | 24.2 | " | C ₇ 0.32 | C ₆ ' 0.013 | 2.4 |
| B3-4 | Slurry | 65 | 330 | TEA 100 | C ₄ 15.2 | C ₄ ' 0.7 | 7.5 |
| B3-5 | " | 65 | 391 | " | " | C ₄ ' 1.8 | 7.2 |
| B3-6 | " | 65 | 408 | " | C ₄ 12.0 | C ₄ ' 4.0 | 5.2 |
| B3-7 | " | 65 | 350 | " | C ₄ 15.2 | C ₄ ' 1.3 | 7.5 |
| B3-8 | " | 65 | 405 | TEA 50 | " | C ₄ ' 1.6 | 8.8 |
| B3-9 | " | 65 | 390 | TEA 100 | " | C ₄ ' 0.20 | 15.0 |

- Cont'd -

Note TEA = triethyl aluminum DEAC = Diethyl aluminum chloride

4-MP-1 = 4-Methylpentene-1 C₂' = Ethylene C₄ = n-ButaneC₆' = Hexene-1 C₇ = n-Heptane

Table 16 (Cont'd)

| C_2' - partial pressure (kg/cm ²) | Polymeri- zation tempera- ture (°C) | Properties | | | |
|--|---|---------------------------------|---------------|--------|-----------------------|
| | | Density (g/cm ³) | [η] (dl/g) | S.C.B. | \bar{M}_w/\bar{M}_n |
| 8.3 | 70 | 0.942 | 0.83 | 15 | 5.5 |
| 10 | 140 | 0.943 | 0.81 | 10 | 3.7 |
| 10 | 140 | 0.940 | 0.82 | 12 | 3.8 |
| 5.0 | 70 | 0.949 | 0.75 | 11 | 5.3 |
| 8.0 | 70 | 0.941 | 0.92 | 14 | 5.4 |
| 4.0 | 50 | 0.910 | 0.82 | 35 | 5.9 |
| 5.0 | 70 | 0.942 | 0.75 | 16 | 5.8 |
| 5.0 | 70 | 0.935 | 0.74 | 20 | 5.9 |
| 1.5 | 70 | 0.949 | 0.27 | 11 | 5.6 |

1 Example 26

A composition of ethylene- α -olefin copolymers was prepared from a two stage polymerization. The first stage polymerization was carried out for 90 min. using 5 the catalyst obtained in Example 1 and triethyl aluminum (co-catalyst) and employing other polymerization conditions shown in Table 17.

Successively the second stage polymerization was conducted for 150 min. by changing only the hydrogen 10 partial pressure and the ethylene partial pressure as shown in table 17. In both stages, the liquid phase molar ratio of ethylene, butene-1 and hydrogen were kept at respective fixed levels. Polymerized quantities in each stage were calculated from quantities of fed ethylene. 15 The total polymer consisted of about 50% by weight of lower molecular weight components. Immediately before the completion of the first stage polymerization, a part of the polymer formed was taken out as a polymer sample 20 of the first stage and measured for its density, intrinsic viscosity, S.C.B. and (weight average molecular weight/ number average molecular weight). Similar measurements were also made for the whole polymer of this two stage polymerization. From the values of the first stage polymer and the whole polymer, the intrinsic viscosity and S.C.B. 25 of the polymer formed in the second stage along were calculated, and they were shown in Table 17. The whole polymer gave: density 0.919 g/cm³, melt index 0.5 g/10 min., melt flow ratio 70, intrinsic viscosity 1.70 dl/g,

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1 S.C.B. 27. The flow characteristics and the solid
physical properties of the whole polymer were shown in
Table 19.

Example 27

5 By mixing the ethylene- α -olefin copolymer A3-1
obtained in Example 24 and the ethylene- α -olefin copoly-
mer B3-1 obtained in Example 25 at a 50/50 weight ratio
and kneading the mixture in a Banbury mixer, a composi-
tion having the density, MI and MFR as shown in Table 18
10 was prepared. The physical properties of this composi-
tion were also shown in Table 18.

For the purpose of comparison, in Table 18
were also shown Comparative examples 15 and 16 using high
pressure polyethylenes of the conventional technique
15 (commercial products Sumikathene® F208-1, F101-1 manu-
factured by Sumitomo Chemical Co., Ltd.) as well as
Comparative example 17 using a low density ethylene- α -
olefin copolymer of the conventional technique.

It is obvious from Table 18 that the copolymer
20 composition of this invention has a Brabender torque about
equal to those of high pressure polyethylenes (good in
processability) and is quite excellent in tensile impact
strength, rigidity, ESCR and tensile strength, compared
with these polyethylenes.

25 When compared with the low density ethylene- α -
olefin copolymer of the conventional technique, this
composition has a much smaller Brabender torque

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1 (processability is much better), a superior tensile
impact strength and tensile strength.

Table 17

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst TEA (mmol) | Solvent (g) | α -olefin (g) | H ₂ partial pressure (kg/cm ²) |
|-----------|-----------------------|------------------------------------|------------------------|------------------------|-------------|----------------------|---|
| 1st stage | Slurry | 5 | 24.3 | 5 | C_4 | 1000 | C_4' 250 |
| 2nd stage | Slurry | | | | | | 14 |

- Cont'd -

Note C_4 = n-Butane TEA = Triethyl aluminum
 C_4' = Butene-1 () = Calculated values

C_2' = Ethylene

Table 17 (Cont'd)

| | | Properties | | | | |
|---|--|--------------------------------------|---------------------------------|---------------|--------|-----------------------|
| C ₂ '- partial pressure (kg/cm ²) | Polymeri- zation temperature (°C) | Polymeri- zation time (min) | Density (g/cm ³) | [η] (dl/g) | S.C.B. | \bar{M}_w/\bar{M}_n |
| 3 | | 90 | 0.900 | 2.6 | 37 | 5.8 |
| 8 | 50 | 150 | - | (0.8) (17) | - | |

Table 18

| Mixing method | Copolymer A | | Copolymer B | | Properties of composition | | | | |
|------------------------|-------------|-------------|-------------|-------------|------------------------------|---------------|-----|-------------------------------|-----|
| | Designation | % by weight | Designation | % by weight | Density (g/cm ³) | MI (g/10 min) | MFR | Distribution index of S.C.B.* | |
| Example 27 | Banbury | A3-1 | 50 | B3-1 | 50 | 0.920 | 0.5 | 70 | 2.5 |
| Comparative Example 15 | - | - | - | - | 0.923 | 1.4 | 50 | - | |
| Comparative Example 16 | - | - | - | - | 0.922 | 0.3 | 65 | - | |
| Comparative Example 17 | - | - | - | - | 0.920 | 0.5 | 30 | - | |

- Cont'd -

$$\text{* Distribution index of S.C.B.} = \frac{(\text{S.C.B. of copolymer A})}{(\text{S.C.B. of copolymer B})}$$

Table 18 (Cont'd)

| Physical properties of composition | | | | |
|---|---|------------------------------|---|----------------------------|
| Tensile impact strength (kg-cm/cm ²) | Olsen's flexural modulus (kg/cm ²) | ESCR F ₅₀ (hr) | Tensile strength (kg/cm ²) | Brabender torque (kg·m) |
| 450 | 2600 | >1000 | 320 | 2.0 |
| 130 | 2400 | 0.3 | 160 | 1.9 |
| 200 | 2200 | 30 | 180 | 2.2 |
| 280 | 3200 | >1000 | 260 | 3.5 |

1 Examples 28 to 31

Compositions having densities, MIs and MFRs shown in Table 19 were obtained, by blending ethylene- α -olefin copolymers A obtained in Example 24 and ethylene- α -olefin copolymers B obtained in Example 25 at mixing ratios as shown in Table 19. The physical properties of these compositions were shown in Table 19.

In Table 19 were also shown a composition of similar ethylene- α -olefin copolymers synthesized in two stage polymerization (Example 26) as well as, for comparison, ethylene- α -olefin copolymers compositions (Comparative examples 18, 19, 20) of which higher molecular weight components have smaller S.C.B. than lower molecular weight components do or have relatively few S.C.B. Also as shown in Table 19 an ethylene- α -olefin copolymers composition (Comparative example 21, to be compared with Examples 30 and 31) of which distribution index of S.C.B. meets the scope of the presen invention but of which lower molecular weight components have too low an intrinsic viscosity.

As is obvious from Table 19, in the compositions of this invention, higher molecular weight components have larger S.C.B. than lower molecular weight components do. (Comparison should be made between Examples 26, 28 and 29 and Comparative example 18, and also between Example 30 and 31 and Comparative examples 19 and 20.) The compositions of this invention are also far superior in tensile impact strength and tensile strength to the Comparative examples.

Table 19

| | Mixing method | Copolymer A | | Copolymer B | | Properties of composition | | |
|------------------------|---------------|-------------|-------------|-------------|-------------|------------------------------|---------------|----------|
| | | Designation | % by weight | Designation | % by weight | Density (g/cm ³) | MI (g/10 min) | MFR |
| Example 26 | - | - | - | - | - | 0.919 | 0.5 | 70 (2.2) |
| Example 28 | Solution | A3-2 | 50 | B3-2 | 50 | 0.920 | 0.5 | 70 2.7 |
| Example 29 | " | A3-3 | 50 | B3-3 | 50 | 0.920 | 0.5 | 70 2.0 |
| Example 30 | Banbury | A3-4 | 50 | B3-4 | 50 | 0.929 | 0.8 | 50 2.0 |
| Example 31 | Solution | A3-5 | 30 | B3-5 | 70 | 0.929 | 0.8 | 50 2.0 |
| Comparative Example 18 | Banbury | A3-6 | 50 | B3-6 | 50 | 0.920 | 0.5 | 70 0.26 |
| Comparative Example 19 | " | A3-7 | 50 | B3-7 | 50 | 0.929 | 0.8 | 50 1.0 |
| Comparative Example 20 | " | A3-8 | 50 | B3-8 | 50 | 0.929 | 0.8 | 50 0.4 |
| Comparative Example 21 | " | A3-9 | 65 | B3-9 | 35 | 0.929 | 0.8 | 50 2.0 |

- Cont'd -

*Distribution index = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)
S.C.B.

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Table 19 (Cont'd)

| Tensile impact strength (kg-cm/cm ²) | Olsen's flexural modulus (kg/cm ²) | Tensile strength (kg/cm ²) | Tackiness |
|--|--|--|-----------|
| 470 | 2500 | 320 | o |
| 550 | 2600 | 340 | o |
| 520 | 2600 | 320 | o |
| 300 | 4000 | 300 | o |
| 280 | 4000 | 290 | o |
| 150 | 3300 | 210 | x |
| 200 | 4200 | 240 | o |
| 90 | 4500 | 200 | o |
| 120 | 4000 | 230 | o |

1 Example 32

The composition prepared in Example 27 and the low density ethylene- α -olefin copolymer of the conventional technique used in Comparative example 17 were subjected 5 to film processing under the following conditions.

Processing conditions

Extruder: Tanabe 30 mm ϕ extruder

Screw: Full flight L/D = 28, C.R. = 2.5

Die: Diameter 50 mm, die gap 2.0 mm

10 Temperature control: C₁ 170°, C₂ 220°, C₃ 220°,
HD 220°C

Screw revolution: 35 rpm

Output: 3.2 kg/hr

Blow up ratio: 2.5

15 Frost line height: 180 mm

Take-off speed: 5 m/min

Film thickness: 35 μ

Also, the commercial high pressure polyethylenes used in Comparative examples 15 and 16 were subjected to 20 film processing under the following conditions.

Die gap: 1.0 mm

Temperature control: C₁ 140°, C₂ 160°, C₃ 160°,
HD 160°C

(Other conditions were same as those applied above.)

25 In the case of the low density ethylene- α -olefin copolymer of the conventional technique used in Comparative example 17, a satisfactory film was not obtained with too much load put on the motor and with

1 shark skin formed on the film surface.

In the cases of the composition prepared in Example 27 and the commercial high pressure polyethylenes used in Comparative examples 15 and 16, satisfactory 5 films were obtained with no excessive motor loads. The physical properties of these films were shown in Table 20. The film of the composition prepared in Example 27 is far superior to those of the high pressure polyethylenes, in dart impact strength, Elmendorf tear 10 strengths (absolute value and MD/TD balance), tensile strength, heat-sealing characteristics, hot tack property and heat sealing strength in contaminated condition.

In the film of the composition prepared in Example 27, heat-sealing strength and heat sealing 15 strength in contaminated condition had about same values, while, in the films of Comparative examples 15 and 16, heat sealing strength in contaminated condition were slightly lower than heat-sealing strength.

The measurement methods of the physical properties shown in table 20 are described below.

Dart impact strength: In accordance with ASTM D 1709A.

Elmendorf tear strength: In accordance with JIS Z 1702.

Tensile strength: In accordance with JIS K 6732-62

25 Heat-sealing characteristics: Heat-sealing strength of a film heat-sealed with a heat sealer of bar type. The maximum heat-sealing strength was obtained when pulled under conditions

1 of film thickness of 35 μ , width of 15 mm
and pulling speed of 200 mm/min. after heat-
sealing under sealing pressure of 1 kg/cm²,
0.5 sec. and each incremental 5°C.

5 Hot tack property: A test sample (25 mm wide and
400 mm long) was folded into two, and the one
end was fixed to the upper clamp and a stripping
weight was placed on the other end.
The area near the crease was inserted between
10 heating bars and heat-sealed under a sealing
pressure of 1 kg/cm² for 0.5 sec., and then
the length of the stripped surface was measured.

Heat Sealing strength in contaminated condition:
This is a test method for evaluating the heat-
15 sealing characteristics in the condition that
the heat-sealed surface is soiled with contents
such as mayonaise, edible oils and flours.
Specifically, a test film sample was folded in
such a way that the surface soiled with an
20 edible oil came inside, and was heat-sealed
under the same conditions as used in heat-
sealing characteristics. Then, its heat-
sealing strength was measured.

Comparative Example 15

25 A commercial high pressure polyethylene
(Sumikathene[®] F208-1 manufactured by Sumitomo Chemical
Co., Ltd.) was subjected to measurements of physical

1 properties and film processing. Results were shown in
Tables 18 and 20.

Comparative Example 16

A commercial high pressure polyethylene
5 (Sumikathene[®] F 101-1 manufactured by Sumitomo Chemical
Co., Ltd.) was subjected to measurements of physical
properties and film processing. Results were shown in
Tables 18 and 20.

Comparative Example 17

10 A low density ethylene- α -olefin copolymer of
the conventional technique was synthesized, using the
catalyst produced in Example 1 and triethyl aluminum
(co-catalyst) and employing the other polymerization
conditions shown in Table 21. The copolymer gave:
15 density 0.920 g/cm³, MI 0.5 g/10 min., MFR 30. The
physical properties of this polymer were shown in
Table 18.

Comparative Examples 18, 19, 20

Compositions of ethylene- α -olefin copolymers
20 of the conventional technique were prepared, by mixing
ethylene- α -olefin copolymers A obtained in Example 24
and ethylene- α -olefin copolymers B obtained in Example
25 at ratios shown in Table 19. In these compositions,
molecular weight distributions are made wider and lower
25 molecular weight components have larger S.C.B. and higher

1 molecular weight components have smaller S.C.B. Densities, MIs, MFRs and physical properties of these compositions were shown in Table 19.

Comparative Example 21

5 By mixing an ethylene- α -olefin copolymer A obtained in Example 24 and an ethylene- α -olefin copolymer B obtained in Example 25 at a ratio as shown in Table 19, a composition of ethylene- α -olefin copolymers were prepared of which distribution index of S.C.B., meets the
10 scope of this invention but of which lower molecular weight weight components have a too low intrinsic viscosity. Its density, MI, MFR and physical properties were shown in Table 19.

Table 20

| | Dart impact strength (kg.cm/mm) | Elmendorf tear strength MD/TD (kg/cm) | Tensile strength MD/TD (kg/cm ²) | Heat-sealing strength (kg/15mm width) | Hot tack property (mm) | Heat sealing strength in contaminated condition; |
|------------------------|---------------------------------|---------------------------------------|--|---------------------------------------|------------------------|--|
| Example 27 | 700 | 120/150 | 450/410 | 1.5 | 1.0 | ○ |
| Comparative Example 15 | 270 | 80/50 | 250/210 | 0.7 | 4.0 | △ |
| Comparative Example 16 | 250 | 70/70 | 280/250 | 0.7 | 3.0 | △ |

Table 21

| Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst TEA (mmol) | Solvent (kg) | α -olefin (kg) | H ₂ partial pressure (kg/cm ²) | C ₂ ' partial pressure (kg/cm ²) | Polymerization temperature (°C) | Polymerization time (min) |
|-----------------------|------------------------------------|------------------------|------------------------|--------------------|-----------------------|---|---|---------------------------------|---------------------------|
| Slurry | 65 | 202 | 100 | C ₄ 7.0 | C ₄ ' 7.16 | 3.0 | 10 | 50 | 90 |

Note TEA = Triethyl aluminum

C₄ = n-Butane

C₄' = Butene-1

C₂' = Ethylene

1 Example 33

Ethylene- α -olefin copolymers A were synthesized using the catalyst produced in Example 1 and organo-aluminum compounds (co-catalyst) and employing α -olefins and other polymerization conditions as shown in Table 22. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these copolymers were shown in Table 22.

These copolymers are used in the following examples as mixing components.

Example 34

Ethylene- α -olefin copolymers B were synthesized using the catalyst produced in Example 1 and organo-aluminum compounds (co-catalyst) and employing α -olefins and other polymerization conditions as shown in Table 23. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these copolymers were shown in Table 23.

These copolymers are used in the following examples as mixing components.

Table 22

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst (mmol) | Solvent (kg) | α -olefin (kg) | H ₂ partial pressure (kg/cm ²) |
|-------|-----------------------|------------------------------------|------------------------|--------------------|---------------------|------------------------|---|
| A4-1 | Slurry | 65 | 310 | TEA 100 | C ₄ 6.0 | C ₄ ' 6.14 | 0.70 |
| A4-2 | Solution | 1 | 24.3 | DEAC 2.5 | C ₇ 0.27 | 4-MP-1 0.090 | 0.15 |
| A4-3 | Slurry | 65 | 83 | TEA 50 | C ₄ 6.0 | C ₄ ' 6.14 | 0.09 |
| A4-4 | " | 65 | 309 | TEA 100 | " | " | 1.2 |
| A4-5 | " | 65 | 145 | TEA 50 | " | " | 0.59 |
| A4-6 | Solution | 1 | 25.2 | DEAC 2.5 | C ₇ 0.30 | C ₆ ' 0.035 | 0.2 |
| A4-7 | Slurry | 65 | 303 | TEA 100 | C ₄ 6.0 | C ₄ ' 6.14 | 0.36 |
| A4-8 | " | 65 | 125 | " | " | " | 1.8 |
| A4-9 | Solution | 1 | 24.5 | DEAC 2.5 | C ₇ 0.40 | 4-MP-1 0.040 | 0.25 |
| A4-10 | Slurry | 65 | 121 | TEA 100 | C ₄ 6.0 | C ₄ ' 3.7 | 1.2 |
| A4-11 | " | 65 | 302 | " | " | C ₄ ' 6.14 | 1.4 |

- Cont'd -

Table 22 (Cont'd)

| C ₂ '- partial pressure (kg/cm ²) | Polymeri- zation tempera- ture (°C) | Properties | | | | Note |
|---|---|---------------------------------|---------------|--------|--------------------------------|----------------------------------|
| | | Density (g/cm ³) | [η] (dl/g) | S.C.B. | M _w /M _n | |
| 7.8 | 50 | 0.912 | 2.6 | 24 | 5.6 | TEA = Triethyl aluminum |
| 20 | 140 | 0.912 | 2.5 | 17 | 3.4 | DEAC = Diethyl aluminum chloride |
| 7.0 | 50 | 0.912 | 4.4 | 20 | 5.8 | C ₄ = n-Butane |
| 3.0 | 50 | 0.911 | 2.2 | 25 | 5.7 | C _{4'} = Butene-1 |
| 6.7 | 50 | 0.906 | 2.6 | 29 | 5.8 | C _{6'} = Hexene-1 |
| 20 | 140 | 0.909 | 2.2 | 18 | 3.4 | C ₇ = n-Heptane |
| 9.0 | 50 | 0.917 | 3.3 | 16 | 5.6 | |
| 18 | 50 | 0.923 | 2.6 | 9 | 5.5 | |
| 20 | 140 | 0.923 | 2.5 | 8 | 3.3 | |
| 20 | 50 | 0.925 | 3.3 | 6 | 5.5 | |
| 8.5 | 50 | 0.913 | 2.1 | 23 | 5.4 | |

Table 23

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst (mmol) | Solvent (kg) | α -olefin (kg) | H ₂ partial pressure (kg/cm ²) |
|-------|-----------------------|------------------------------------|------------------------|--------------------|---------------------|------------------------|---|
| B4-1 | Slurry | 65 | 402 | TEA 50 | C ₄ 12.0 | C ₄ ' 3.2 | 7.8 |
| B4-2 | Solution | 1 | 24.2 | DEAC 2.5 | C ₇ 0.80 | 4-MP-1 0.045 | 2.2 |
| B4-3 | Slurry | 65 | 405 | TEA 50 | C ₄ 12.0 | C ₄ ' 3.2 | 7.0 |
| B4-4 | " | 65 | 425 | " | C ₄ 15.2 | C ₄ ' 2.0 | 10.5 |
| B4-5 | " | 65 | 411 | " | " | C ₄ ' 1.6 | 6.5 |
| B4-6 | Solution | 1 | 25.1 | DEAC 2.5 | C ₇ 0.82 | C ₆ ' 0.017 | 2.7 |
| B4-7 | Slurry | 65 | 346 | TEA 100 | C ₄ 15.2 | C ₄ ' 1.1 | 12 |
| B4-8 | " | 65 | 408 | " | C ₄ 12.0 | C ₄ ' 4.0 | 5.2 |
| B4-9 | Solution | 1 | 24.9 | DEAC 2.5 | C ₇ 0.28 | 4-MP-1 0.055 | 2.0 |
| B4-10 | Slurry | 65 | 250 | TEA 100 | C ₄ 15.2 | C ₄ ' 0.4 | 13.5 |
| B4-11 | " | 65 | 410 | TEA 50 | " | C ₄ ' 1.4 | 12 |
| B4-12 | " | 65 | 290 | " | C ₄ 6.0 | C ₄ ' 6.14 | 8.1 |

- Cont'd -

Table 23 (Cont'd)

| C_2' - partial pressure (kg/cm ²) | Polymer- ization tempera- ture (°C) | Properties | | | | Note |
|--|---|---------------------------------|---------------|--------|-----------------------|----------------------------------|
| | | Density (g/cm ³) | [n] (dl/g) | S.C.B. | \bar{M}_w/\bar{M}_n | |
| 6 | 70 | 0.929 | 0.85 | 24 | 5.8 | TEA = Triethyl aluminum |
| 10 | 140 | 0.929 | 0.81 | 17 | 3.6 | DEAC = Diethyl aluminum chloride |
| 6 | 70 | 0.928 | 0.90 | 24 | 5.7 | 4-MP-1 = 4-Methylpenten-1 |
| 5 | 70 | 0.929 | 0.65 | 25 | 5.7 | C_4 = n-Butane |
| 5 | 70 | 0.935 | 0.83 | 20 | 5.5 | C_4' = Butene-1 |
| 10 | 140 | 0.926 | 0.63 | 18 | 3.5 | C_6' = Hexene-1 |
| 3 | 70 | 0.941 | 0.52 | 16 | 5.4 | C_7 = n-Heptane |
| 4 | 50 | 0.910 | 0.82 | 35 | 5.9 | |
| 10 | 140 | 0.912 | 0.85 | 22 | 3.7 | |
| 1.5 | 50 | 0.930 | 0.28 | 25 | 5.7 | |
| 3 | 70 | 0.934 | 0.53 | 22 | 5.8 | |
| 9 | 50 | 0.927 | 1.2 | 23 | 5.7 | |

1 Example 35

A composition of ethylene- α -olefin copolymers was prepared in two stage polymerization. The first stage polymerization was carried out for 70 min. using 5 the catalyst produced in Example 1 and triethyl alminum (co-catalyst) and other polymerization conditions as shown in Table 24. Successively the second stage polymerization was conducted for 180 min. by changing only the hydrogen partial pressure and the ethylene partial 10 pressure as shown in Table 24. In both stages, the liquid phase molar ratio of ethylene, butene-1 and hydrogen was kept at respective fixed levels. The polymerized quantities in each stage were calculated from the quantities of fed ethylene. The copolymers consisted of about 50% 15 by weight of higher molecular weight components and about 50% by weight of lower molecular weight components.

Immediately before the completion of the first stage polymerization, a part of the polymer was taken out and measured for its density, intrinsic viscosity, S.C.B. 20 and (weight average molecular weight/number average molecular weight). The whole polymer obtained after the second stage was also measured for the same test items. From the values of the first stage polymer and the whole polymer, the intrinsic viscosity and S.C.B. of the poly- 25 mer formed in the second stage alone were calculated. These values were shown in Table 24. The whole polymer gave: density 0.921 g/cm³, MI 0.5 g/10 min., MFR 70, intrinsic viscosity 1.7 dl/g, S.C.B. 24. Flow

1 characteristics and solid physical properties of the whole
polymer were shown in Table 26.

Example 36

By mixing the ethylene- α -olefin copolymer A4-1
5 obtained in Example 33 and the ethylene- α -olefin copolymer
B4-1 obtained in Example 34 at a 50/50 weight ratio and
kneading the mixture in a Banbury mixer, a composition
of ethylene- α -olefin copolymers having the density, MI
and MFR shown in Table 25 was prepared. Physical pro-
10 perties of this composition were also shown in Table 25.

For comparison, in Table 25 were also shown Comparative
examples 15 and 16 using high pressure polyethylenes of
the conventional technique (commercial product

15 Sumikathene[®] F 208-1, F 101-1 manufactured by Sumitomo
Chemical Co., Ltd.) as well as Comparative example 17
using a low density ethylene- α -olefin copolymer of the
conventional technique.

As is obvious from Table 25, the polymer com-
position of the present invention, when compared with high
20 pressure polyethylenes, has about an equal Brabender
torque (satisfactory in processability), and is much
superior in tensile impact strength, rigidity, ESCR and
tensile strength, and further is about equally satis-
factory in transparency.

25 Compared with the low density ethylene- α -olefin
copolymer of the conventional technique, this polymer
composition has a much lower Brabender torque (far

1 excellent in processability) and a higher tensile impact
strength and tensile strength.

Examples 38, 39, 40, 41, 42, 43

By mixing the ethylene- α -olefin copolymers A
5 obtained in Example 33 and the ethylene- α -olefin copoly-
mers B obtained in Example 34 at ratios as shown in
Table 26, compositions having densities, MIs and MFRs
shown in Table 26 were obtained. Physical properties of
these compositions were also shown in Table 26.

10 In Table 26 were also shown a similar composi-
tion prepared by two stage polymerization (Example 35)
and, for the purpose of comparison, compositions of low
density ethylene- α -olefin copolymers of the conventional
technique (Comparative examples 22, 23, 25) of which
15 molecular weight distributions are made wider and of
which lower molecular weight components have larger S.C.B.
and of which higher molecular weight components have
smaller S.C.B. In Table 26 was also shown a composition
of ethylene- α -olefin copolymers (Comparative example 24,
20 to be compared with Examples 40 and 42) of which distri-
bution index of S.C.B. meets the scope of this invention
but of which lower molecular weight components have a
too low intrinsic viscosity.

As seen in Table 26, in the compositions of this
25 invention, S.C.B. of higher molecular weight components
are more than or about equal to those of lower molecular
weight components. (Compare Examples 35, 38 and 41 with

1 Comparative examples 22 and 23, and Example 43 with Comparative example 25.) Therefore, compared with the compositions of the conventional technique, the compositions of this invention are far excellent in tensile
5 impact strength and tensile strength, and are superior in transparency.

From the comparison between Comparative example 17 of Table 25 and Comparative example 22 of Table 26, it is learned that widening of molecular weight distribution (higher MFR gives wider distribution) in the manufacture of a low density ethylene- α -olefin copolymer of the conventional technique with its density and MI kept constant results in large reduction in tensile impact strength and tensile strength.

15 From the comparison of Examples 40 and 42 with Comparative example 24, it is learned that a too low intrinsic viscosity of lower molecular weight components badly affects its tensile impact strength, tensile strength and transparency.

Table 24

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst TEA (mmol) | Solvent (g) | α -olefin (g) | H_2 partial pressure (kg/cm^2) |
|-----------|-----------------------|------------------------------------|------------------------|------------------------|-------------|----------------------|--------------------------------------|
| 1st stage | Slurry | 5 | 24.3 | 5 | C_4 1000 | C_4 , 250 | 0.6 |
| 2nd stage | Slurry | | | | | | 10 |

- Cont'd -

TEA = Triethyl aluminum

Note C_4 = n-Butane C_4' = Butene-1 () = Calculated values C_2' = Ethylene

Table 24 (Cont'd)

| C_2' - partial pressure (kg/cm ²) | Polymeri- zation tempera- ture (°C) | Polymeri- zation time (min.) | Properties | | | |
|--|---|---------------------------------------|---------------------------------|---------------|--------|-----------------------|
| | | | Density (g/cm ³) | [η] (dl/g) | S.C.B. | \bar{M}_w/\bar{M}_n |
| 4 | 50 | 70 | 0.912 | 2.6 | 24 | 5.7 |
| 5 | | 180 | - | (0.8) | (23) | - |

Table 25

| Mixing method | Copolymer A | | Copolymer B | | Properties of composition | | | |
|------------------------|--|-------------|-------------|-------------|------------------------------|----------------|-----|-------------------------------|
| | Designation | % by weight | Designation | % by weight | Density (g/cm ³) | MI (g/10 min.) | MFR | Distribution index of S.C.B.* |
| Example 36 | Banbury | A4-1 | 50 | B4-1 | 50 | 0.920 | 0.5 | 70 |
| Example 37 | " | A4-11 | 50 | B4-12 | 50 | 0.921 | 0.7 | 40 |
| Comparative Example 15 | High pressure polyethylene (Sumikathene R F208-1) | | | | 0.923 | 1.4 | 50 | - |
| Comparative Example 16 | " (Sumikathene R F101-1) | | | | 0.922 | 0.3 | 65 | - |
| Comparative Example 17 | Low density ethylene/ α -olefin copolymer of the conventional technique | | | | 0.920 | 0.5 | 30 | - |

- Cont'd -

$$\text{* Distribution index} = \frac{(\text{S.C.B. of copolymer A})}{(\text{S.C.B. of copolymer B})}$$

Table 25 (Cont'd)
Physical properties of composition

| Tensile impact strength (kg-cm/cm ²) | Olsen's flexual modulus (kg/cm ²) | ESCR T ₅₀ (hr) | Tensile strength (kg/cm ²) | Haze (%) | Brabender torque (kg·m) |
|---|--|---------------------------------|---|-------------|----------------------------|
| 350 | 2800 | >1000 | 280 | 5 | 2.0 |
| 370 | 3000 | >1000 | 290 | 5 | 2.6 |
| 130 | 2400 | 0.3 | 160 | 4 | 1.9 |
| 200 | 2200 | 30 | 180 | 6 | 2.2 |
| 280 | 3200 | >1000 | 260 | 5 | 3.5 |

Table 26

| | Mixing method | Copolymer A | | Copolymer B | | Properties of composition | | |
|--|---------------|-------------|-------------|-------------|-------------|------------------------------|----------------------------------|----------|
| | | Designation | % by weight | Designation | % by weight | Density (g/cm ³) | MI (g/cm ³ , 10 min.) | MFR |
| Example 35 - Two stage polymerization - | | | | | | | | |
| Example 38 | Solution | A4-2 | 50 | B4-2 | 50 | 0.920 | 0.5 | 70 (1.0) |
| Example 39 | " | A4-3 | 30 | B4-3 | 70 | 0.921 | 0.6 | 70 1.0 |
| Example 40 | Banbury | A4-4 | 50 | B4-4 | 50 | 0.920 | 1.1 | 65 0.8 |
| Example 41 | " | A4-5 | 50 | B4-5 | 50 | 0.920 | 0.5 | 90 1.0 |
| Example 42 | Solution | A4-6 | 50 | B4-6 | 50 | 0.920 | 1.1 | 65 1.5 |
| Example 43 | Banbury | A4-7 | 50 | B4-7 | 50 | 0.929 | 0.2 | 100 1.0 |
| Comparative Example 22 | " | A4-8 | 50 | B4-8 | 50 | 0.920 | 0.5 | 70 0.26 |
| Comparative Example 23 | Solution | A4-9 | 50 | B4-9 | 50 | 0.920 | 0.6 | 65 0.36 |
| Comparative Example 24 | Banbury | A4-4 | 65 | B4-10 | 35 | 0.920 | 0.8 | 50 1.0 |
| Comparative Example 25 | " | A4-10 | 50 | B4-11 | 50 | 0.930 | 0.2 | 100 0.27 |

* Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

- Cont'd -

Table 26 (Cont'd)

| Physical properties of composition | | | | |
|--|--|--|----------|-----------|
| Tensile impact strength (kg-cm/cm ²) | Olsen's flexural modulus (kg/cm ²) | Tensile strength (kg/cm ²) | Haze (%) | Tackiness |
| 340 | 2800 | 280 | 6 | o |
| 430 | 2800 | 320 | .5 | o |
| 370 | 2800 | 300 | 7 | o |
| 290 | 2800 | 250 | 6 | o |
| 400 | 2700 | 300 | 8 | o |
| 360 | 2800 | 310 | 5 | o |
| 370 | 4200 | 300 | 8 | o |
| 150 | 3300 | 210 | 12 | x |
| 180 | 3200 | 220 | 12 | Δ |
| 130 | 2800 | 220 | 15 | o |
| 170 | 4800 | 230 | 20 | o |

1 Example 44

The compositions prepared in Examples 36 and 37 as well as the low density ethylene- α -olefin copolymer of the conventional technique used in Comparative example 5 17 were subjected to film processing in the same conditions as used in Example 32.

The commercial high pressure polyethylenes used in Comparative examples 15 and 16 were also subjected to film processing in the same conditions. A satisfactory 10 film was not obtained from the low density ethylene- α -olefin copolymer of the conventional technique used in Comparative example 17, with too much load put on the motor and with shark skin formed on the film surface.

Satisfactory films having good transparency 15 were obtained from the compositions prepared in Examples 36 and 37 and the commercial high pressure polyethylenes used in Comparative examples 15 and 16, with no problem of motor load. Physical properties of these films were shown in 'Table 27'. Compared with the films of the high 20 pressure method polyethylenes, the films of the compositions prepared in Examples 36 and 37 had about same transparency but were largely excellent in dart impact strength, Elmendorf tear strength (absolute value property and MD/TD balance), heat-sealing properties, tensile 25 strength, hot tack and heat sealing strength in contaminated condition. In case of the films of the compositions prepared in Examples 36 and 37, heat-sealing strengths and heat sealing strength in contaminated condition were at

1 about same levels, but in the films of the high pressure
polyethylenes of Comparative example 16, heat sealing
strength in contaminated condition were lower than heat-
sealing strengths.

5 Comparative Examples 22, 23, 25

By mixing ethylene- α -olefin copolymers A obtained in Example 33 and ethylene- α -olefin copolymers B obtained in Example 34 at ratios as shown in Table 26, compositions of low density ethylene- α -olefin copolymers 10 of the conventional technique were prepared of which molecular weight distribution are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B. Densities, MIs, MFRs and physical properties of 15 these compositions were shown in Table 26.

Comparative Example 24

By mixing an ethylene- α -olefin copolymer A obtained in Example 33 and an ethylene- α -olefin copolymer B obtained in Example 34 at a ratio shown in Table 26, 20 a composition of ethylene- α -olefin copolymers was prepared of which distribution index of S.C.B. meets the scope of this invention but of which lower molecular weight components have a too low intrinsic viscosity. Its density, MI, MFR and physical properties were shown in Table 26.

Table 27

| | Haze (%) | Dart impact strength (kg·cm/mm) | Elmendorf tear strength MD/TD (kg/cm) | Tensile strength MD/TD (kg/cm ²) | Heat-sealing strength (kg/15mm width) | Hot tack property (mm) | Heat sealing strength in contaminated condition |
|---------------------------|-------------|--|---|---|--|------------------------------|--|
| Example 36 | 5 | 500 | 90/120 | 410/380 | 1.2 | 2.0 | 0 |
| Example 37 | 5 | 450 | 60/120 | 420/370 | 1.3 | 2.0 | 0 |
| Comparative Example 15 | 4 | 270 | 80/50 | 250/210 | 0.7 | 4.0 | Δ |
| Comparative Example 16 | 7 | 250 | 70/70 | 280/250 | 0.7 | 3.0 | Δ |

1 Example 45

Ethylene- α -olefin copolymers were synthesized using the catalyst produced in Example 1 and organo-aluminum compounds (co-catalyst) and employing α -olefins and other polymerization conditions as shown in Table 28. Densities, intrinsic viscosities, and S.C.B. of these copolymers were shown in Table 28.

These copolymers are used in the following examples as higher molecular weight components.

10 Example 46

Ethylene- α -olefin copolymers were synthesized using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing α -olefins and other polymerization conditions as shown in Table 29. Densities, intrinsic viscosities and S.C.B. of these copolymers were shown in Table 29.

These copolymers are used in the following examples as lower molecular weight components.

Table 28

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst (mmol) | Solvent (kg) | α -olefin (kg) | H ₂ partial pressure (kg) |
|-----|-----------------------|------------------------------------|------------------------|--------------------|----------------------|-----------------------|--------------------------------------|
| A-1 | Slurry | 65 | 131 | TEA 100 | C ₄ ' 6.0 | C ₄ ' 6.14 | 0.45 |
| A-2 | " | 65 | 145 | TEA 50 | " | " | 0.59 |
| A-3 | " | 65 | 310 | TEA 100 | " | " | 0.70 |
| A-4 | " | 65 | 125 | " | " | " | 1.8 |
| A-5 | Solution | 1 | 25.3 | DEAC 2.5 | C ₇ 0.25 | 4-MP-1 0.11 | 0.1 |
| A-6 | " | 1 | 24.5 | " | C ₇ 0.30 | 4-MP-1 0.05 | 0.15 |
| A-7 | Slurry | 65 | 121 | TEA 50 | C ₄ ' 6.0 | C ₄ ' 6.14 | 0.98 |
| A-8 | " | 65 | 320 | TEA 100 | " | " | 3.0 |

Note TEA = Triethyl aluminum

C₄' = n-Butane

DEAC = Diethyl aluminum chloride

C₄' = Butene-1

4-MP-1 = 4-Methylpentene-1

C₇ = n-Heptane

- Cont'd -

Table 28 (Cont'd)

| | | Properties | | | |
|---|---|---------------------------------|---------------|--------|--|
| C ₂ '- partial pressure (kg/cm ²) | Polymeri- zation tempera- ture (°C) | Density (g/cm ³) | [n] (dl/g) | S.C.B. | |
| 5.0 | 50 | 0.899 | 2.6 | 38 | |
| 6.7 | 50 | 0.906 | 2.6 | 29 | |
| 7.8 | 50 | 0.912 | 2.6 | 24 | |
| 18 | 50 | 0.923 | 2.6 | 9 | |
| 20 | 140 | 0.904 | 2.5 | 23 | |
| 20 | 140 | 0.920 | 2.5 | 10 | |
| 6.5 | 50 | 0.907 | 2.2 | 30 | |
| 20 | 50 | 0.928 | 2.2 | 8 | |

Table 29

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst (mmol) | Solvent (kg) | α -olefin (kg) | H_2 partial pressure (kg/cm^2) |
|-----|-----------------------|------------------------------------|------------------------|--------------------|--------------|-----------------------|--------------------------------------|
| B-1 | Slurry | 65 | 405 | TEA 50 | C_4 50' | C_4' 2.0 | 10.8 |
| B-2 | " | 65 | 411 | " | C_4 15.2 | C_4' 1.6 | 6.5 |
| B-3 | " | 65 | 402 | " | C_4 12.0 | C_4' 3.2 | 7.8 |
| B-4 | " | 65 | 408 | TEA 100 | " | C_4' 4.0 | 5.2 |
| B-5 | Solution | 1 | 26.5 | DEAC 2.5 | C_7 0.28 | 4-MP-1 0.03 | 3.0 |
| B-6 | " | 1 | 25.7 | " | C_7 0.25 | 4-MP-1 0.05 | 2.5 |
| B-7 | Slurry | 65 | 407 | TEA 100 | C_4 15.4 | C_4' 0.5 | 13.0 |
| B-8 | " | 65 | 422 | TEA 50 | C_4 15.2 | C_4' 1.8 | 11.0 |

- Cont'd -

 C_4 = n-Butane C_4' = Butene-1 C_7 = n-Heptane

Note TEA = Triethyl aluminum

DEAC = Diethyl aluminum chloride

4-MP-1 = 4-Methylpentene-1

Table 29 (Cont'd)

| C_2' - partial pressure (kg/cm ²) | Polymeriza- tion tempera- ture (°C) | Properties | | |
|--|---|---------------------------------|---------------|--------|
| | | Density (g/cm ³) | [η] (dl/g) | S.C.B. |
| 8.3 | 70 | 0.912 | 0.83 | 15 |
| 5 | 70 | 0.935 | 0.83 | 20 |
| 6 | 70 | 0.929 | 0.85 | 24 |
| 4 | 50 | 0.910 | 0.82 | 35 |
| 10 | 140 | 0.938 | 0.50 | 13 |
| 10 | 140 | 0.912 | 0.52 | 22 |
| 5 | 70 | 0.953 | 0.62 | 9 |
| 5 | 70 | 0.934 | 0.61 | 22 |

1 Example 47

A composition of ethylene- α -olefin copolymers was prepared in two stage polymerization. The first stage polymerization was carried out for 70 min. using 5 the catalyst produced in Example 1 and triethyl aluminum (co-catalyst) and other polymerization conditions as shown in Table 30. Successively, the second stage polymerization was conducted for 180 min. by changing only the hydrogen partial pressure and the ethylene partial 10 pressure as shown in Table 30. In both stages, the liquid phase molar ratio of ethylene, butene-1 and hydrogen was kept constant at respective fixed levels. The polymerized quantities in each stage were calculated from the quantities of fed ethylene. The copolymer com- 15 position consisted of about 50% by weight of higher molecular weight components and about 50% by weight of lower molecular weight components. Immediately before the completion of the first stage polymerization, a part of the polymer was taken out and measured for its density, 20 intrinsic viscosity and S.C.B. The whole polymer obtained after the second stage was also measured for the same test items. From the values of the first stage polymer and the whole polymer, the intrinsic viscosity and the number of branched short chains of the polymer formed in the 25 second stage alone were calculated. These values were shown in Table 30. The whole polymer gave: density 0.921 g/cm³, MI 0.5 g/10 min., MFR 70, intrinsic viscosity 1.7 dl/g, S.C.B. 24, g^*_η 0.93. The whole polymer was subjected

1 to gel permeation chromatography and a curve of molecular
weight distribution shown in Fig. 4 was obtained.

Because of bimodal distribution which has two peaks, the curve was divided into two parts using broken
5 lines. The areas of each part were calculated, and the lower molecular weight components and the higher molecular weight components were determined to be 48 and 52% by weight, respectively.

The whole polymer was divided into 30 fractions
10 using column chromatography. These fractions were divided into two parts (the lower molecular weight components and the higher molecular weight components) so that the former became 48% by weight and the latter 52% by weight.
S.C.B., densities and intrinsic viscosities of each component were shown in Table 32.

Flow characteristics and solid physical properties of the whole polymer were shown in Table 33.

In the following examples, ethylene- α -olefin copolymers as higher molecular weight components and
20 ethylene- α -olefin copolymers as lower molecular weight components were mixed at respective fixed ratios (total quantity 1 kg) and kneaded for 5 min. with a Banbury mixer (150 to 230 rpm). At that time, replacement by nitrogen was conducted completely and the polymer
25 temperatures were controlled not to exceed 250°C.

When sample quantities were small, mixing was made in xylene. After mixing, the whole solution was added into methanol to cause precipitation. After

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1 filtration, the precipitate was completely dried in a
vacuum drier and used as a copolymers composition sample.

Examples 48, 49, 50

Ethylene- α -olefin copolymers obtained in
5 Example 45 and ethylene- α -olefin copolymers obtained in
Example 46 were kneaded with a Banbury mixer at ratios
as shown in Table 31.

Thus, compositions of copolymers having densities,
MIs, MFRs, intrinsic viscosities, S.C.B. and g_{η}^* shown in
10 Table 32 were obtained. These compositions had molecular
weight distribution curves about equal to Fig. 4. With
the same technique as used in Example 47, quantities of lower
molecular weight components and higher molecular weight com-
ponents were calculated, and they were both approximately
15 50% by weight as shown in Table 32. Physical properties of
these compositions were shown in Table 33.

With the same technique as used in Example 47,
column fractionation was applied in order to divide into
higher molecular weight components and lower molecular
20 weight components. Characteristics of the components
were shown in Table 32.

In Tables 32 and 33 were also shown Example 47
using a composition of ethylene- α -olefin copolymers pre-
pared in two stage polymerization and, for comparison,
25 Comparative example 26 using a high pressure method poly-
ethylene of the conventional technique (commercial
product Sumikathene[®] F 101-1 manufactured by Sumitomo

1 Chemical Co., Ltd.), Comparative example 27 using a com-
position of low density ethylene- α -olefin copolymers of
the conventional technique and Comparative example 28
using a composition of low density ethylene- α -olefin
5 copolymers of the conventional technique of which
moelcular weight distribution is made wider and of which
lower molecular weight components have larger S.C.B. and
of which higher molecular weight components have smaller
S.C.B.

10 As is obvious from Tables 32 and 33, when com-
pared with the high pressure polyethylene, the copolymer
compositions of this invention have about equivalent
Brabender torques (excellent in processability), and are
largely excellent in tensile impact strength, rigidity,
15 ESCR and tensile strength. Transparency is equally good,
because distribution index of S.C.B. is in a certain range
as defined by the present invention. When compared with
the composition of low density ethylene- α -olefin copoly-
mers of the conventional technique, the compositions of
20 this invention have far smaller Brabender torques (much
better processability) and higher tensile impact
strengths and tensile strengths.

From comparison between Comparative examples 27
and 28 in Tables 32 and 33, it is learned that widening
25 of molecular weight distribution (larger MFR gives wider
distribution) in the manufacture of a low density
ethylene- α -olefin copolymer of the conventional technique
with density and MI fixed results in large reduction in
tensile impact strength and tensile strength.

Table 30

| No. | Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst TEA (mmol) | Solvent (g) | α -olefin (g) | H ₂ partial pressure (kg/cm ²) |
|-----------|-----------------------|------------------------------------|------------------------|------------------------|-------------|----------------------|---|
| 1st stage | Slurry | 5 | 24.3 | 5 | C_4 | 1000 | 0.6 |
| 2nd stage | Slurry | | | | C_4' | 250 | 10 |

- Cont'd -

Note C_4 = n-Butane TEA = Triethyl aluminum C_4' = Butene-1 () = Calculated values C_2' = Ethylene

Table 30 (Cont'd)

| C_2 '- partial pressure (kg/cm ²) | Polymeri- zation tempera- ture (°C) | Polymeri- zation time (min) | Properties | | |
|--|---|--------------------------------------|---------------------------------|---------------|--------|
| | | | Density (g/cm ³) | [η] (dl/g) | S.C.B. |
| 4 | 50 | 70 | 0.912 | 2.6 | 24 |
| | | 180 | - | (0.8) | (23) |
| 5 | | | | | |

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Table 31

| | Higher molecular weight component | | Lower molecular weight component | |
|------------------------|--------------------------------------|-------------|-------------------------------------|-------------|
| | Designation | % by weight | Designation | % by weight |
| Example 48 | A-1 | 50 | B-1 | 50 |
| Example 49 | A-2 | 50 | B-2 | 50 |
| Example 50 | A-3 | 50 | B-3 | 50 |
| Comparative Example 28 | A-4 | 50 | B-4 | 50 |

Table 32

| | Properties of copolymer | | | | |
|------------------------|---------------------------------|-------------------|-----|------|------------------|
| | Density (g/cm ³) | MI (g/10 min.) | MFR | [η] | S.C.B. (dl/g) |
| Example 47 | 0.921 | 0.5 | 70 | 1.7 | 24 |
| Example 48 | 0.920 | 0.5 | 70 | 1.7 | 26 |
| Example 49 | 0.920 | 0.5 | 70 | 1.7 | 25 |
| Example 50 | 0.920 | 0.5 | 70 | 1.7 | 24 |
| Comparative Example 26 | 0.922 | 0.3 | 65 | 1.06 | 23 |
| Comparative Example 27 | 0.920 | 0.5 | 30 | 1.7 | 23 |
| Comparative Example 28 | 0.920 | 0.5 | 70 | 1.7 | 22 |

- Cont'd -

* Distribution index = $\frac{\text{Degree of S.C.B. of higher molecular weight component}}{\text{Degree of S.C.B. of lower molecular weight component}}$

Degree of S.C.B. of higher molecular weight component
Degree of S.C.B. of lower molecular weight component

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Table 32 (Cont'd)

| Length of main peak chain (A) | | Ratio (% by weight) | |
|----------------------------------|-----------------------------------|----------------------------------|-----------------------------------|
| Lower molecular weight component | Higher molecular weight component | Lower molecular weight component | Higher molecular weight component |
| 1.7 x 10 ³ | 3.4 x 10 ³ | 48 | 52 |
| 1.7 x 10 ³ | 3.4 x 10 ³ | 48 | 52 |
| 1.6 x 10 ³ | 3.5 x 10 ³ | 47 | 53 |
| 1.9 x 10 ³ | 3.4 x 10 ³ | 48 | 52 |
| 1.05 x 10 ³ | 6.5 x 10 ³ | 36 | 64 |
| Uniform distribution (peak) | | 50 | 50 |
| 2.8 x 10 ³ | 3.6 x 10 ³ | 49 | 51 |
| 1.6 x 10 ³ | | | |

- Cont'd -

Table 32 (Cont'd)

| Characteristics of components fractionated by column fractionation | | | | | | |
|--|------------------------------|-----------------------------------|--------|------------------------------|-------------------------------|-----|
| Lower molecular weight component | | Higher molecular weight component | | | Distribution index of S.C.B.* | |
| S.C.B. | Density (g/cm ³) | [n] (dl/g) | S.C.B. | Density (g/cm ³) | [n] (dl/g) | |
| 30 | 0.920 | 0.8 | 18 | 0.915 | 2.6 | 0.6 |
| 27 | 0.924 | 0.8 | 25 | 0.910 | 2.6 | 0.9 |
| 28 | 0.923 | 0.7 | 20 | 0.914 | 2.5 | 0.7 |
| 30 | 0.920 | 0.8 | 18 | 0.915 | 2.5 | 0.6 |
| 27 | 0.916 | 0.6 | 19 | 0.926 | 1.4 | 0.7 |
| 38 | 0.906 | 1.1 | 8 | 0.925 | 2.4 | 0.2 |
| 37 | 0.907 | 0.8 | 7 | 0.926 | 2.6 | 0.2 |

Table 33

| | Physical properties of copolymer | | | | | | |
|------------------------|--|--|--|----------|---------------|---------------|-----------|
| | Tensile impact strength (kg-cm/cm ²) | Olsen's Flexural modulus (kg/cm ²) | Tensile strength (kg/cm ²) | Haze (%) | Torque (kg-m) | ESCR F50 (hr) | Tackiness |
| Example 47 | 340 | 2800 | 280 | 5 | 2.0 | >1000 | 0 |
| Example 48 | 450 | 2600 | 320 | 20 | 2.0 | >1000 | 0 |
| Example 49 | 400 | 2700 | 300 | 8 | 2.0 | >1000 | 0 |
| Example 50 | 350 | 2800 | 280 | 5 | 2.0 | >1000 | 0 |
| Comparative Example 26 | 200 | 2200 | 180 | 6 | 2.2 | 30 | 0 |
| Comparative Example 27 | 280 | 3200 | 260 | 8 | 3.5 | >1000 | 0 |
| Comparative Example 28 | 150 | 3300 | 210 | 12 | 2.0 | >1000 | x |

1 Examples 51, 52

Compositions of ethylene- α -olefin copolymers were prepared by mixing ethylene- α -olefin copolymers obtained in Example 45 and ethylene- α -olefin copolymers 5 obtained in Example 46 at ratios shown in Table 34. Densities, MIs, MFRs, $[\eta]$, S.C.B. and g_{η}^* of these compositions were shown in Table 35. Their physical properties were shown in Table 36.

Molecular weight distributions of Examples 51 10 and 52 showed "one almost symmetrical mountain" curves. The curve in Fig. 5 is that of Example 52. Column fractionation was applied with the same technique as used in Example 47. Its results were shown in Table 35.

In Tables 35 and 36 were also shown low density 15 ethylene- α -olefin copolymers of the conventional technique (Comparative examples 29 and 30) of which molecular weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller 20 S.C.B.

Curves of molecular weight distributions of Comparative examples 29 and 30 were similar to those of Examples 51 and 52. As seen from Tables 35 and 36, in the compositions of this invention, S.C.B. of higher 25 molecular weight components and those of lower molecular weight components are nearly equal (compare Example 51 with Comparative example 29, and also Example 52 with Comparative example 30), therefore, the compositions

1 of the present invention are far superior to the copolymers
of the conventional technique in tensile impact strength
and tensile strength.

Comparative Example 26

5 A commercial high pressure polyethylene
(Sumikathene[®] F 101-1 manufactured by Sumitomo Chemical
Co., Ltd.) was subjected to measurements of physical
properties and. Results were shown in Table 33.

This polyethylene has low η^* of 0.48 and it
10 suggests that this sample has many long chain branches.
Its molecular weight distribution curve was shown in
Fig. 6. Column fractionation was applied with the same
technique as used in Example 47. The fractions obtained
were divided into two groups so that the lower molecular
15 weight component group and the higher molecular weight
component group became about 36 and 64% by weight, res-
pectively. Densities, S.C.B. and intrinsic viscosity of
each group were measured and results were shown in
Table 32.

20 Comparative Example 27

A low density ethylene- α -olefin copolymer of
the conventional technique was synthesized using the
catalyst produced in Example 1, triethyl aluminum (co-
catalyst) and other polymerization conditions as shown
25 in Table 37. The copolymer gave: density 0.920 g/cm³,
MI 0.5 g/10 min., MFR 30, intrinsic viscosity 1.7 dl/g,

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1 S.C.B. 23, η^* 0.95. Its physical properties were shown
in Table 33. Its molecular weight distribution showed
"one almost symmetrical mountain" curve, as seen in
Fig. 1. From the area ratio, the lower molecular weight
5 components and the higher molecular weight components
were determined to be both 50% by weight. Column frac-
tionation was applied with the same technique as used
in Example 47 and results were shown in Table 32.

Comparative Example 28

10 By mixing the ethylene- α -olefin copolymer A-4
obtained in Example 45 and the ethylene- α -olefin copolymer
B-4 obtained in Example 46 at the ratio as given in Table
31, a composition of low density ethylene- α -olefin
copolymers of the conventional technique was prepared of
15 which molecular weight distribution is made wider and
of which lower molecular weight components have larger
S.C.B. and of which higher molecular weight components
have smaller S.C.B. Its density, MI, MFR, $[\eta]$, and η^*
were shown in Table 32. The molecular weight distribu-
20 tion curve of this composition was almost equal to that
in Fig. 4. With the same technique as used in Example 47,
the ratio of the lower and higher molecular weight com-
ponents was determined. Column fractionation was also
conducted. These results were shown in Table 32.
25 Physical properties of this composition were shown in
Table 33.

1 Comparative Examples 29, 30

By mixing ethylene- α -olefin copolymers obtained in Example 45 and ethylene- α -olefin copolymers obtained in Example 46 at ratios as shown in Table 34, compositions 5 of low density ethylene- α -olefin copolymers of the conventional technique were prepared of which molecular weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller 10 S.C.B. Densities, MIs, MFRs, $[n]$, S.C.B. and g_n^* of these compositions were shown in Table 35. Physical properties of these compositions were shown in Table 36.

Table 34

| | Higher molecular weight component | Lower molecular weight component | | |
|------------------------|-----------------------------------|----------------------------------|-------------|-------------|
| | Designation | % by weight | Designation | % by weight |
| Example 51 | A-5 | 60 | B-5 | 40 |
| Example 52 | A-7 | 50 | B-7 | 50 |
| Comparative Example 29 | A-6 | 60 | B-6 | 40 |
| Comparative Example 30 | A-8 | 50 | B-8 | 50 |

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Table 35 (Cont'd)

| Length of main peak chain (A) | | Ratio (% by weight) | |
|--|-----------------------------------|----------------------------------|-----------------------------------|
| Lower molecular weight component | Higher molecular weight component | Lower molecular weight component | Higher molecular weight component |
| Uniform distribution (peak) 2.5 x 10 ³ | | 57 | 43 |
| Uniform distribution (peak) 1.6 x 10 ³ | | 48 | 52 |
| Uniform distribution (peak) 2.5 x 10 ³ | | 58 | 42 |
| Uniform distribution (peak) 1.6 x 10 ³ | | 48 | 52 |

- Cont'd -

Table 35
Properties of copolymer

| | Density (g/cm ³) | MI (g/10 min) | MFR (dl/g) | [η] | S.C.B. | * g _η |
|------------------------|---------------------------------|------------------|---------------|-----|--------|---------------------|
| Example 51 | 0.920 | 0.5 | 70 | 1.7 | 19 | 0.91 |
| Example 52 | 0.929 | 1.2 | 70 | 1.4 | 20 | 0.95 |
| Comparative Example 29 | 0.919 | 0.5 | 70 | 1.7 | 17 | 0.96 |
| Comparative Example 30 | 0.929 | 1.2 | 70 | 1.4 | 17 | 0.93 |

- Cont'd -

$\frac{\text{Degree of S.C.B. of higher}}{\text{molecular weight component}}$
 $\text{of S.C.B.} = \frac{\text{Degree of S.C.B. of lower}}{\text{molecular weight component}}$

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Table 35 (Cont'd)
 Characteristics of components fractionated
 by column fractionation

| S.C.B. Lower molecular weight component | Higher molecular weight component | | | | Distribution index of S.C.B.* |
|---|--------------------------------------|---------------|--------|---------------------------------|-------------------------------------|
| | Density (g/cm ³) | [η] (dl/g) | S.C.B. | Density (g/cm ³) | |
| 22 | 0.933 | 0.5 | 15 | 0.920 | 2.4 |
| 20 | 0.935 | 0.6 | 20 | 0.915 | 2.2 |
| 24 | 0.930 | 0.5 | 7 | 0.927 | 2.4 |
| 29 | 0.922 | 0.6 | 6 | 0.930 | 2.1 |

Table 36

| | Physical properties of copolymer | | | |
|------------------------|--|--|--|-----------|
| | Tensile impact strength (kg.cm/cm ²) | Olsen's Flexural modulus (kg/cm ²) | Tensile strength (kg/cm ²) | Tackiness |
| Example 51 | 480 | 2600 | 320 | o |
| Example 52 | 250 | 3700 | 250 | o |
| Comparative Example 29 | 200 | 3100 | 200 | x |
| Comparative Example 30 | 70 | 4500 | 200 | o |

* Table 37

| Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Co-catalyst TEA (mmol) | Solvent (kg) | α -olefin (kg) | H ₂ partial pressure (kg/cm ²) | C_2' partial pressure (kg/cm ²) | Polymerization temperature (°C) | Polymerization time (min) |
|-----------------------|------------------------------------|------------------------|------------------------|--------------|-----------------------|---|---|---------------------------------|---------------------------|
| Slurry | 65 | 202 | 100 | C_4 | C_4' | 7.0 | 7.16 | 3.0 | 10 50 ; 90 |

Note TEA = Triethyl aluminum

C_4 = n-Butane

C_2' = Ethylene

C_4' = Butene-1

1 Reference Example 1

An ethylene- α -olefin copolymer was synthesized from ethylene and butene-1, using the catalyst produced in Example 1, diethyl aluminum monochloride (co-catalyst) 5 and other polymerization conditions as shown in Table 38. Properties of this copolymer were shown in Table 39. By applying column fractionation, the copolymer was fractionated into fractions of different molecular weights. Then, distribution of S.C.B. against molecular 10 weight was examined as shown in Fig. 7.

In column fractionation, about 5 g of the sample was placed in a fractionation column after being adsorbed on a carrier (Celite 745) in xylene. Then, the column was heated to 130°C, and butyl cellosolve and xylene 15 were passed through the column with the mixing ratio being gradually changed in order to obtain a gradual increase in solvency. Thus, all the copolymer fractions of lower to higher molecular weight were separated. To the eluates was added methanol to cause precipitation 20 of the copolymers. After recovery, the polymers were dried under reduced pressure and each copolymer fraction was obtained. In the above column fractionation process, in order to prevent the possible decomposition of the copolymers, 100 ppm of Irganox® 1076 was added to the 25 original sample and further air inside the column was replaced by nitrogen. Using each copolymer fraction, pressed sheets having about 100 to 300 μ thickness were prepared, and S.C.B. of each copolymer fraction were

1 calculated by conducting Fourier-transform infrared
absorption spectroscopy. Molecular weights of each
copolymer fraction were calculated, using intrinsic
viscosities [η] measured in tetralin of 135°C and the
5 following formula.

$$[\eta] = 5.1 \times 10^{-4} : \bar{M}_n^{0.725}$$

Reference Example 2

With ethylene- α -olefin copolymers of the conventional technique, a relationship between melt index
10 (MI) and tensile impact strength was examined with melt flow ratio (MFR) used as a parameter. Results were shown
in Fig. 8. It is revealed that widening of molecular weight distribution results in remarkable reduction in
tensile impact strength. (In the figure, molecular weight
15 distribution was represented by MFR. Larger MFR means wider molecular weight distribution.). These ethylene- α -olefin copolymers were subjected to molecular weight fractionation with the same technique as used in
Reference Example 1. All the copolymers showed trends
20 similar to that of Reference Example 1. The fractions were divided into two groups (lower molecular weight group and higher molecular weight group) in such a way that each group became about 50% by weight, and (S.C.B. of higher molecular weight component/S.C.B. of lower
25 molecular weight component) was calculated. It was below 0.5 in all the copolymers.

1 Reference Example 3

With a high pressure method polyethylene of the conventional technique and a linear, high density polyethylene of medium to low pressure method, correlations between melt index (MI) and intrinsic viscosity [η] were examined and shown in Fig. 9. The correlation lines of each sample are clearly divided by a partition line (broken line). It is learned that the high pressure polyethylene has much lower intrinsic viscosity than that of the linear high density polyethylene of the same melt index.

A correlation between melt index and intrinsic viscosity was examined with the ethylene- α -olefin copolymers of the present invention. All of the copolymers of the present invention fell in the zone of the linear, high density polyethylene.

Table 38

| Polymerization method | Polymerization vessel capacity (l) | Catalyst quantity (mg) | Solvent (g) | α -olefin (g) | H_2 partial pressure (kg/cm ²) | C_2' partial pressure (kg/cm ²) | Polymerization temperature (°C) | Polymerization time (min) |
|-----------------------|------------------------------------|------------------------|-------------|----------------------|--|---|---------------------------------|---------------------------|
| Solution | 1 | 25.1 | C_7 300 | C_4 1 | 40 | 3.5 | 20 | 140 |

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Table 39

| Properties | | | |
|---------------------------------|------------------|-----|--------|
| Density (g/cm ³) | MI (g/10 min) | MFR | S.C.B. |
| 0.924 | 4 | 25 | 20 |

WHAT IS CLAIMED IS:

1. An ethylene- α -olefin copolymer composition excellent in strength and having a density of 0.910 to 0.940 g/cm³, a melt index of 0.02 to 50 g/10 min. and a melt flow ratio of 35 to 250, which comprises 10 to 70% by weight of an ethylene- α -olefin copolymer A and 90 to 30% by weight of an ethylene- α -olefin copolymer B; said copolymer A being a copolymer of ethylene and an α -olefin of 3 to 18 carbon atoms and having a density of 0.895 to 0.935 g/cm³, an intrinsic viscosity of 1.2 to 6.0 dl/g, and the number of short chain branching per 1000 carbon atoms (hereinafter referred to as "S.C.B.") of 7 to 40; said copolymer B being a copolymer of ethylene and an α -olefin of 3 to 18 carbon atoms and having a density of 0.910 to 0.955 g/cm³, an intrinsic viscosity of 0.3 to 1.5 dl/g, and S.C.B. of 5 to 35; said copolymer A and said copolymer B being selected in order to satisfy a condition that (S.C.B. of said copolymer A)/(S.C.B. of said copolymer B) is at least 0.6.
2. An ethylene- α -olefin copolymer composition according to Claim 1, wherein both of said copolymers A and B have (weight average molecular weight)/(number average molecular weight) of 2 to 10.
3. An ethylene- α -olefin copolymer composition according to Claim 1 or 2, wherein at least one of said copolymer A and said copolymer B is one member selected from the group consisting of an ethylene-butene-1 copolymer, an ethylene-4-methyl-pentene-1 copolymer, an ethylene-

hexene-1 copolymer and an ethylene-octene-1 copolymer.

4. An ethylene- α -olefin copolymer composition excellent in transparency and strength according to Claim 1, 2, or 3, wherein said copolymers A and B are selected in order to satisfy a condition that (S.C.B. of copolymer A)/(S.C.B. of copolymer B) is 0.6 to 1.7.

5. An ethylene- α -olefin copolymer composition according to Claim 1, 2, 3, or 4, wherein said copolymer composition is prepared by a multi-stage polymerization.

6. An ethylene- α -olefin copolymer composition according to Claim 1, 2, 3, or 4, characterized in that said copolymer components are mixed as a result of a two stage polymerization wherein, in the first stage, said copolymer A is polymerized under certain polymerization conditions for a certain length of time and successively, in the second stage, said copolymer B is polymerized with the first stage polymerization conditions changed other than catalysts until an intended weight ratio of copolymers A and B is obtained.

7. A composition of copolymers of ethylene and an α -olefin of 3 to 18 carbon atoms, having the following properties:

- (1) density of 0.910 to 0.940 g/cm³,
- (2) intrinsic viscosity $[\eta]$ of 0.7 to 4.0 dl/g,
- (3) melt index of 0.02 to 50 g/10 min.,
- (4) S.C.B. being 5 to 45,
- (5) $[\eta]/[\eta]_L$ namely g_{η}^* being at least 0.8, where $[\eta]_L$ is an intrinsic viscosity of a linear polyethylene

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having the same weight average molecular weight measured by a light scattering method, and

(6) (S.C.B. of the higher molecular weight components)/(S.C.B. of the lower molecular weight components) being at least 0.6, where these two components groups are obtained by a molecular weight fractionation method.

8. A copolymer composition according to Claim 7, wherein (S.C.B. of the higher molecular weight components)/(S.C.B. of the lower molecular weight components) is 0.6 to 0.8.

9. A copolymer composition according to Claim 7 which gives a two-peak or multi-peak molecular weight distribution curve when subjected to gel permeation chromatography, in which curve the total lower molecular weight components contain at least one component having a peak chain length of 2×10^2 to 3.0×10^3 Å and the total higher molecular weight components contain at least one component having a peak chain length of 1×10^3 to 6×10^4 Å and the former components occupy 70 to 30% by weight of the total copolymers and the latter components 30 to 70% by weight.

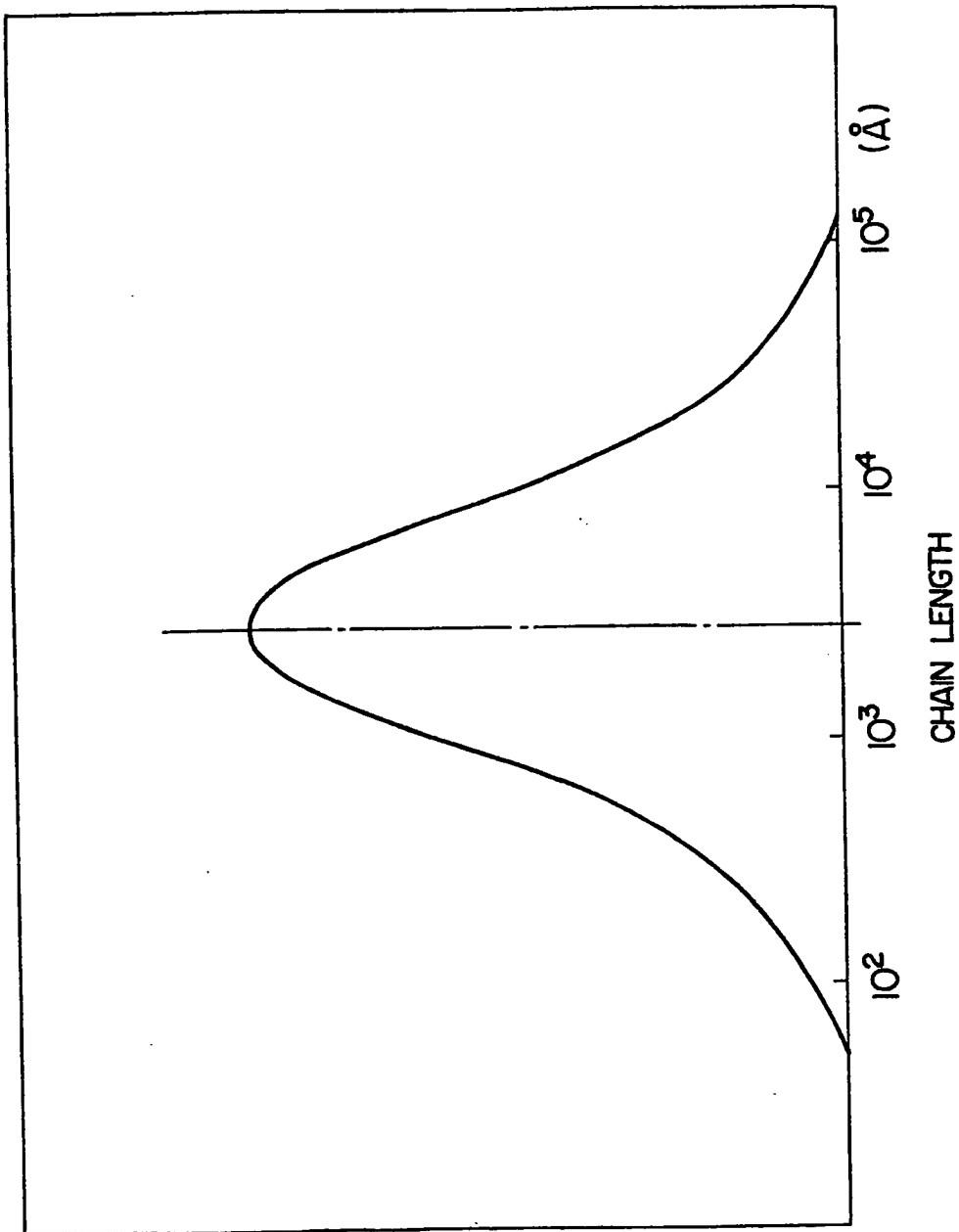
10. A copolymer composition according to Claims 7 to 9, wherein the α-olefin is butene-1 and/or 4-methyl-pentene-1 and/or hexene-1 and/or octene-1.

11. A copolymer composition according to Claims 7 to 10 which is obtained from a multi-stage polymerization using a carrier-supported Ziegler catalyst.

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FIG. I

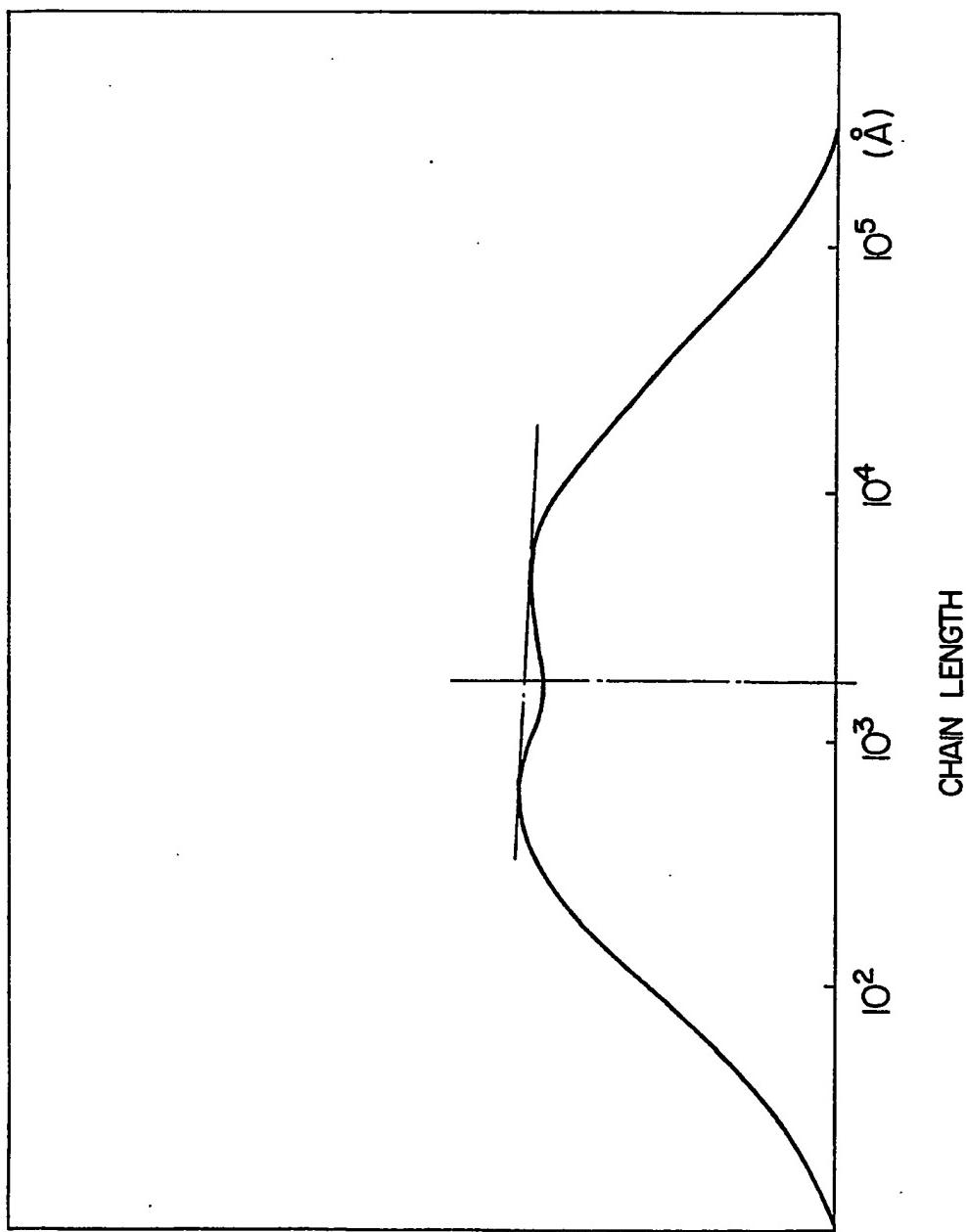


WEIGHT FRACTION

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FIG. 2

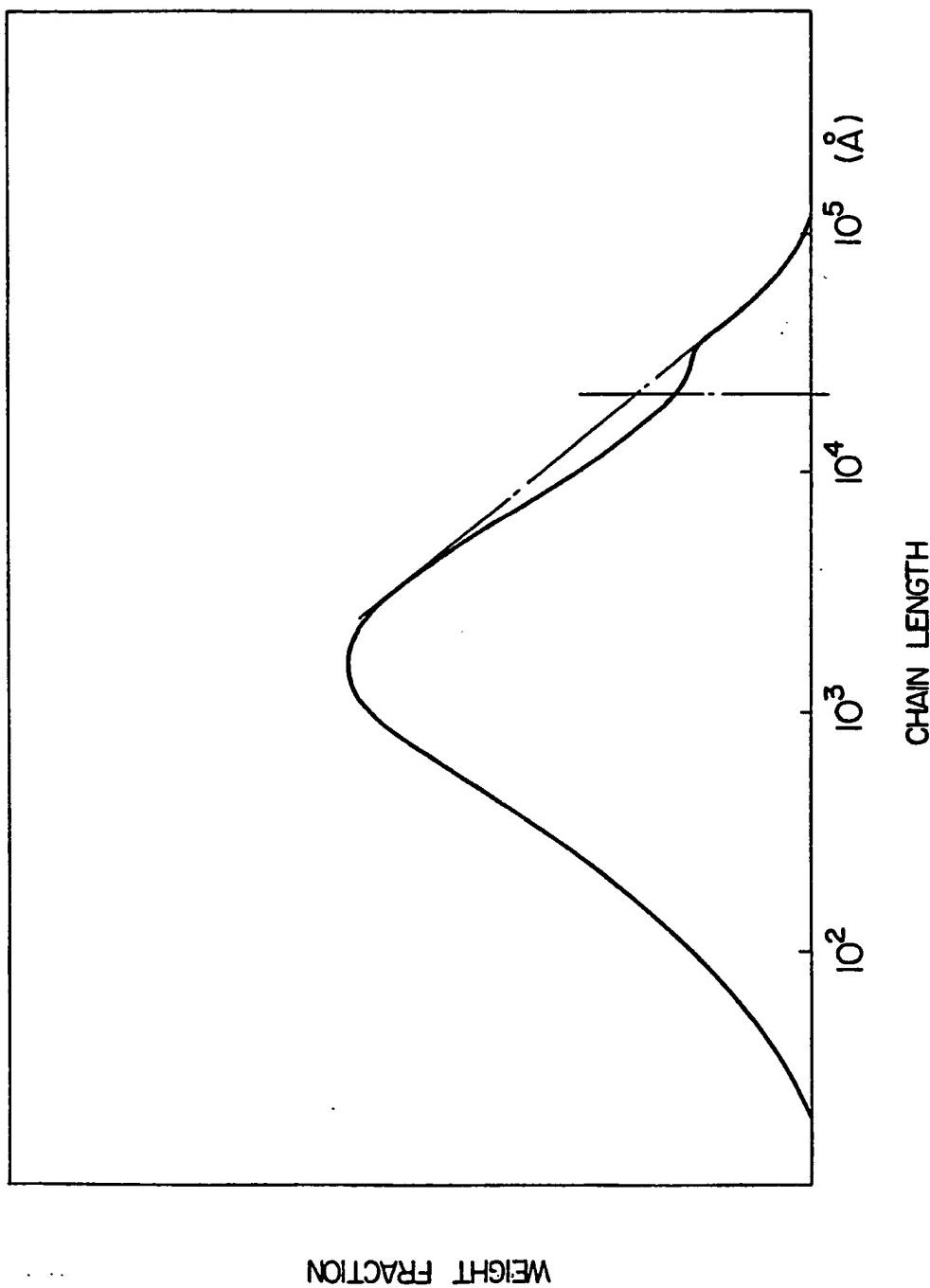


WEIGHT FRACTION

0057891

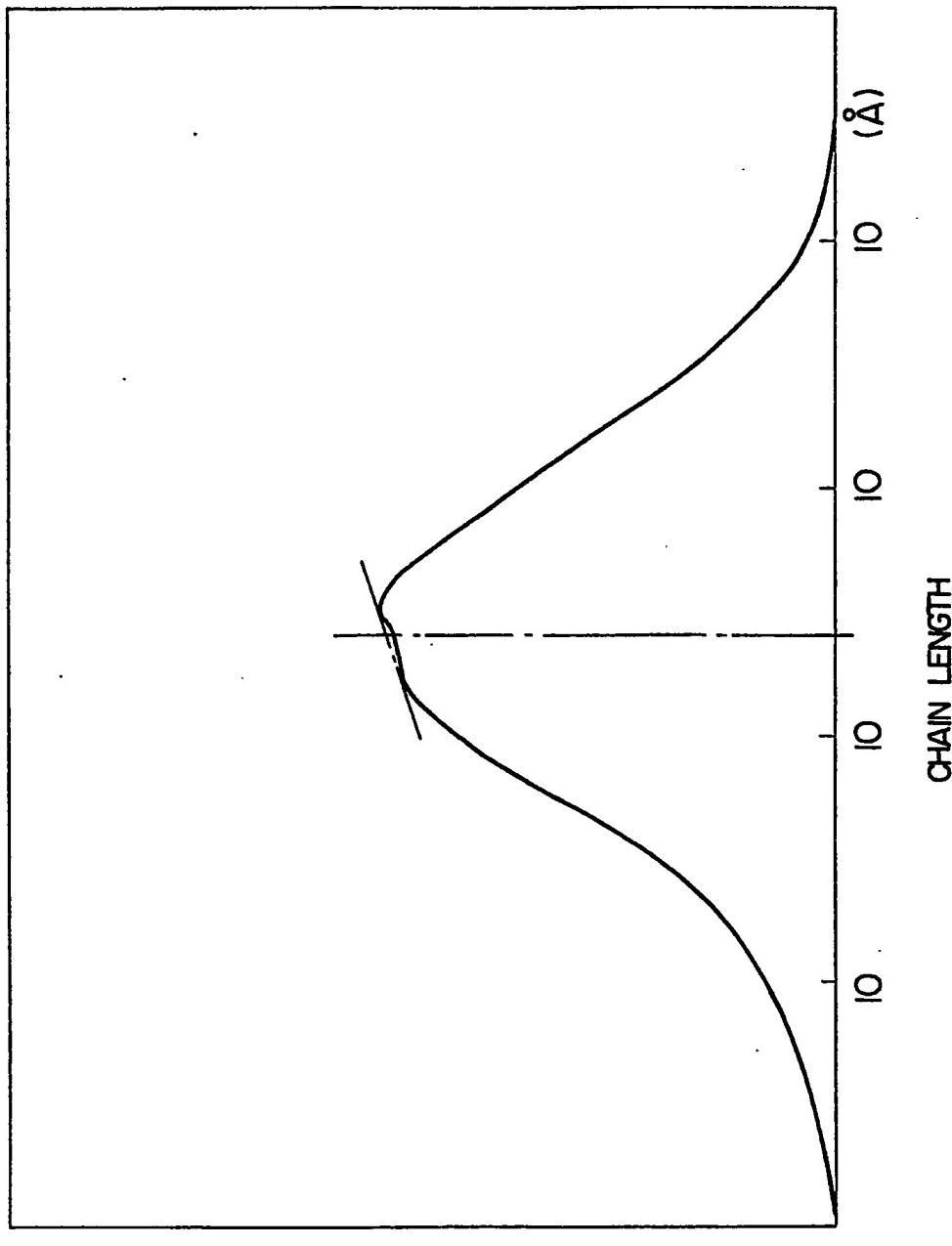
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FIG. 3



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FIG. 4

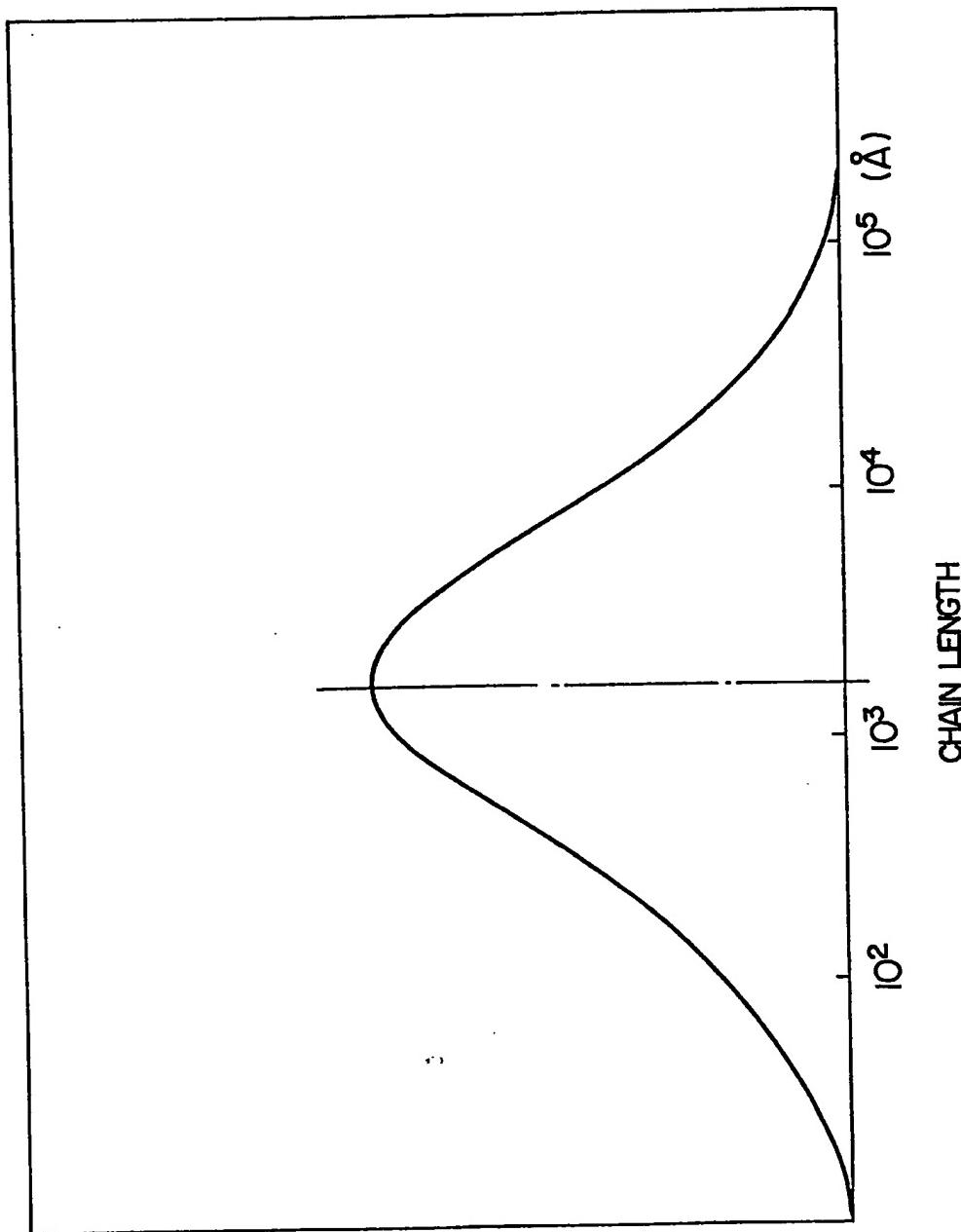


WEIGHT FRACTION

0057891

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FIG. 5

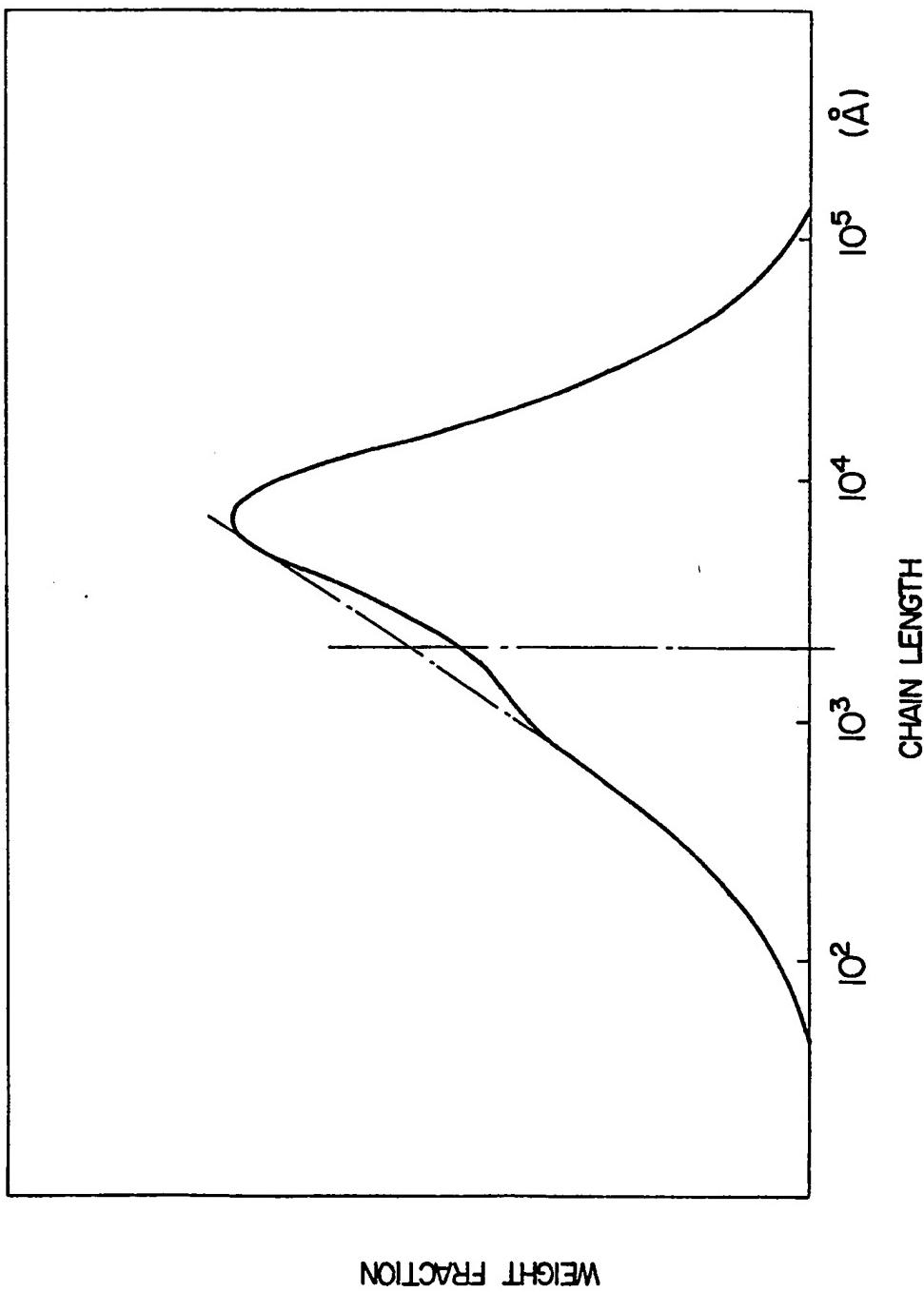


WEIGHT FRACTION

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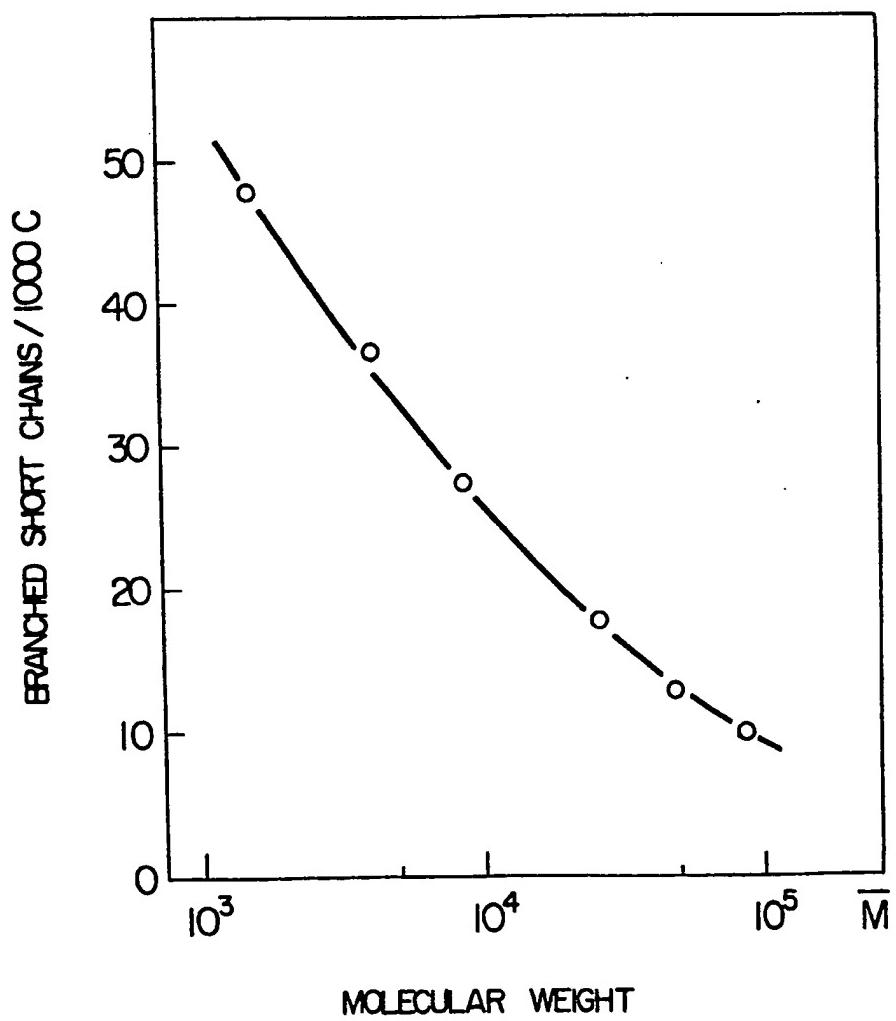
FIG. 6



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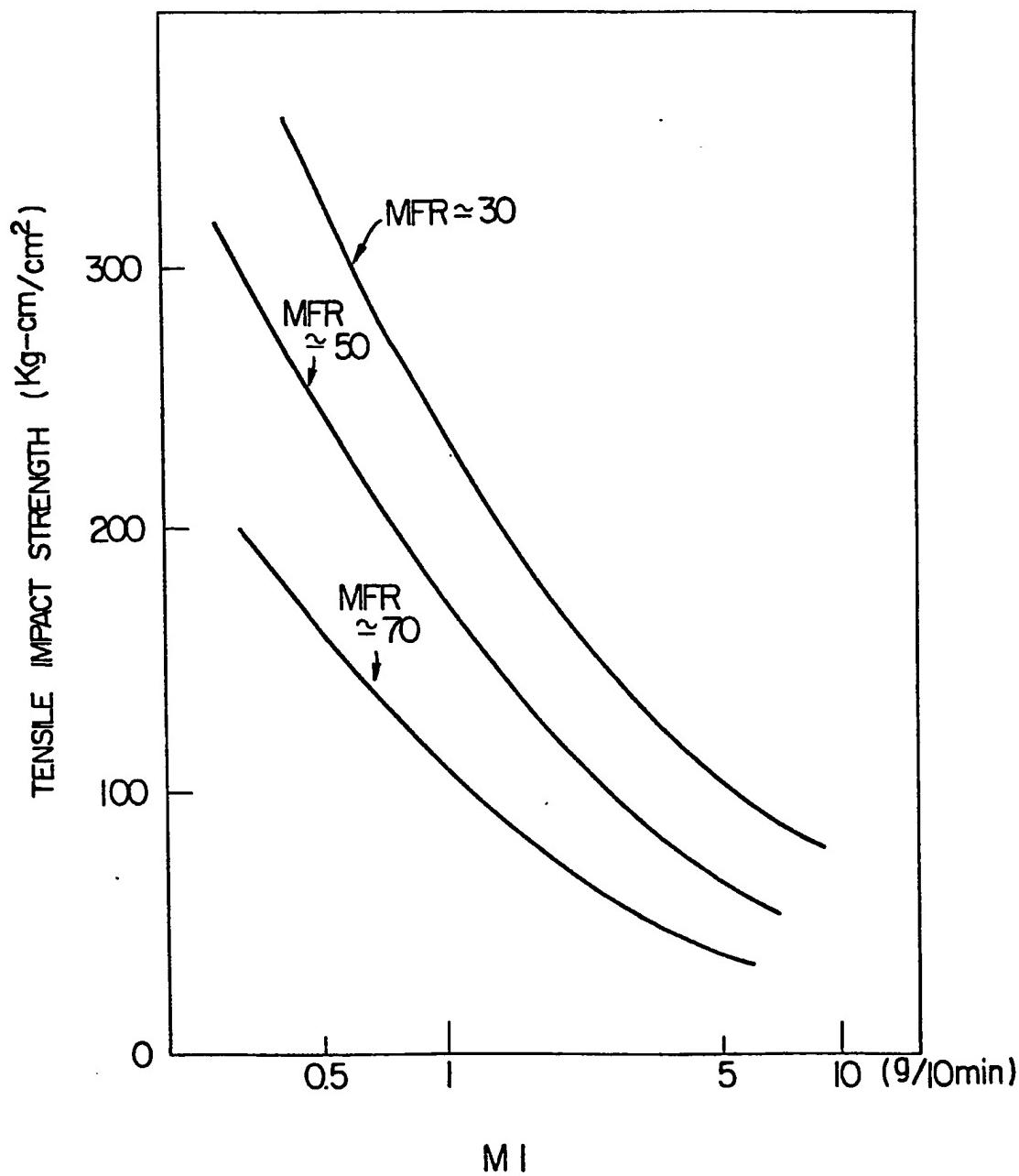
FIG. 7



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FIG. 9

